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THE

PHYSICAL REVIEW.

NATURAL AND MAGNETIC ROTATORY DISPERSION IN THE INFRA-RED SPECTRUM.

By L. R. Ingersoll.

Introduction.

In spite of the large amount of investigation which has been carried out on the rotation of the plane of polarization by naturally active substances for wave-lengths of the visible spectrum and to a certain extent in the ultra-violet, apparently nothing has hitherto been done on the infra-red side save in the case of the one substance, quartz.

Hussel,[1] using the phosphoro-photographic method of Lommel made measurements of the rotatory dispersion of this crystal to wave-length 1μ, while Carvallo,[2] Dongier[3] and others,[4] using modifications of the original method of Desains,[5] extended this spectral region to beyond 2μ. In none of these investigations, however, were other substances studied, possibly because of the difficulties involved in measuring the much smaller rotations usually found in materials other than quartz.

By a slight modification of the method and apparatus already developed and used by the writer[6] for measuring magnetic rotation in the early infra-red it has been found possible to determine the rotation of naturally active substances as well, in this spectral region, and with an accuracy at least comparable with that of the best visual observations. This is sufficient to handle even substances of small rotatory power, and accordingly the rotatory dispersion of several organic liquids and solutions,

[1] A. Hussel, Wied. Ann., 43, p. 498 (1891).

[2] E. Carvallo, Comptes Rendus, 114, p. 288 (1892).

[3] R. Dongier, Comptes Rendus, 125, p. 228 (1897) & 126, p. 1627 (1898).

[4] G. Moreau, Ann. Chim. Phys., 30, p. 433 (1893), and A. Hupe, Wied. Ann. Beib., 19, p. 501 (1895).

[5] P. Desains, Pogg. Ann., 128, p. 487 (1866).

[6] Phil. Mag. (6), 11, p. 41 (1906), and 18, p. 74 (1909). Phys. Rev., 23, p. 489 (1906).

as well as of quartz, has been determined for the spectral region in which it is possible to work with this method, viz., from about the *D* lines to a little beyond 2μ. In some cases supplementary visual observations have been made to carry the series farther towards the blue end of the spectrum.

Magnetic rotation measurements on these substances have also been made at the same time to add further evidence on Wiedemann's law of the proportionality of magnetic and natural rotations for different wave-lengths. This law, first enunciated by G. Wiedemann[1] in 1851 as the result of experiments on turpentine for a series of five Fraunhofer lines, has been the subject of some controversy. Disch[2] concluded from experiments on ethyl valerate and quartz that it holds approximately for the visible spectrum, but more recently Darmois[3] finds that for a number of compounds of the terpene series, at any rate, the law does not hold at all. He concludes that Wiedemann's relation, then, was the result of pure chance and has no longer any significance. Very recently, however, Lowry[4] in the course of an extremely careful investigation of the rotatory dispersion of quartz finds that the law applies with great accuracy for this material over the range of spectrum ($\lambda = .43\mu$ to $.67\mu$) which he has been able to investigate. He suggests that its validity may be confined to crystals and that active liquids may constitute exceptions.

It becomes, then, a matter of considerable interest to test this law further, over the greatest possible spectral range and with an experimental arrangement which shall afford identical conditions (of wave-length, temperature, part of crystal used, etc.) for each series of measurements.

Temperature coefficients of both natural and magnetic rotation have also been determined in one or two cases in the present work, with the view of attempting to decide whether or not these coefficients depend on the wave-length. Soret and Sarasin[5] found an apparent increase of the natural coefficient for quartz in the shorter wave-lengths. Molby[6] has also recently found indications of the same thing over the range from room to liquid air temperatures. On the other hand, v. Lang,[7] Sohncke[8] and Gumlich[9] have not been able to draw any such conclusions, their results on this crystal pointing to an independence of wave-length.

[1] G. Wiedemann, Pogg. Ann., 82, p. 215 (1851).
[2] J. Disch, Ann. d. Phys., 12, p. 1153 (1903).
[3] E. Darmois, Ann. Chim. Phys., 22, p. 495 (1911).
[4] T. M. Lowry, Phil. Trans., 212, p. 261 (1913).
[5] Soret and Sarasin, Sur la Polarisation Rotatoire du Quartz, Geneva, 1882.
[6] F. A. Molby, PHYS. REV., 31, p. 291 (1910).
[7] V. v. Lang, Sitzungsber. d. k. Ges. d. Wiss. zu Wien, 71, p. 707 (1875).
[8] L. Sohncke, Wied. Ann., 3, p. 516 (1878).
[9] E. Gumlich, Wied. Ann., 64, p. 333 (1898).

It has seemed worth while, then, to supplement these observations with measurements over the six-fold greater spectral region which the writer has investigated, and to extend them to the magnetic rotation as well; also to test one or two other substances in addition to quartz.

METHOD AND APPARATUS.

The method need be outlined only briefly as it has—save for the slight but essential modification which admits of its application to the measurement of natural rotations—been already described in previous papers by the writer.[1] The general disposition of the apparatus is evident from

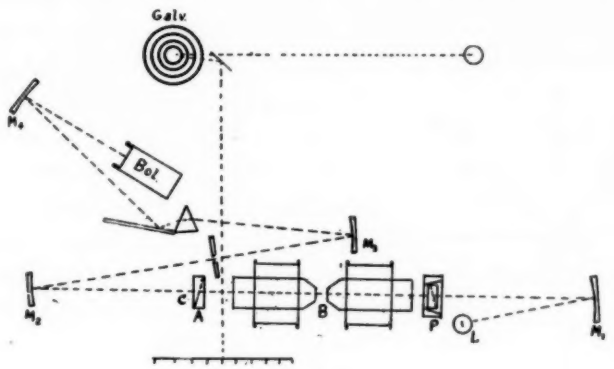

Fig. 1.

Fig. 1. Light from the flat strip tungsten lamp L,[2] after reflection from M_1 is polarized by P, transmitted down the axis of the electromagnet, and, after division into two beams by the (double image prism) analyzer A, falls on the slit of the spectrometer. The two images on the slit, of mutually perpendicular planes of polarization, form two spectra on the strips of the differential bolometer which is connected with a sensitive Thomson galvanometer. If the polarizer is oriented so that its plane makes an angle of 45° with each of the principal planes of the analyzer the intensity of radiation on each strip of bolometer will be the same and the galvanometer will show no deflection: but if a rotation is produced, as by a cell with sugar solution placed at B, a galvanometer deflection will result which may be used to measure such rotation. The magnetic rotation produced by exciting the electromagnet is obviously measurable in the same way.

[1] Loc. cit., particularly Phil. Mag., 18, p. 77 (1909).

[2] These lamps were specially made and furnished for this investigation through the kindness of Director E. P. Hyde of the Nela Research Laboratory. They give a line source many times more brilliant than the Nernst glower formerly used and of great constancy. Without them the present work would have been practically impossible.

A modification of the method as already mentioned will be seen to be necessary for the present work from the following considerations: Magnetic rotation, being produced by merely exciting the magnet, does not involve in the process of measurement any shift of the substance under test, *i. e.*, its removal from the field. Natural rotation, on the other hand, obviously cannot be produced or reversed in this simple way and it would seem to be necessary to remove the test cell entirely to get the zero from which the rotation is to be measured. This, however, must be avoided if possible as it is almost certain to involve slight shifts of the beam of light and a consequent lack of uniformity accompanied by a spurious galvanometer deflection.

To avoid this, the polarizer, which was mounted in a large divided circle, was arranged so that it could be rotated exactly 90° between stops. Fig. 2 shows almost at a glance the results of such rotation. The original plane of polarization P being rotated by the substance through the small angle θ, gives unequal components on the two principal planes of the analyzing double image prism. A rotation of the polarizer to P' will exactly interchange these two components and a doubled galvanometer deflection will result. The process is analogous to reversing the direction of the field in measuring magnetic rotations.

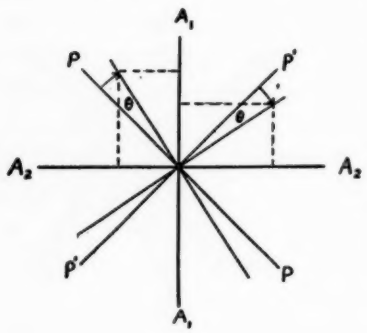

Fig. 2.

To interpret these galvanometer deflections in terms of degrees and minutes of rotation by the active substance, the polarizer was turned by a measured amount—usually about 3 degrees—and a comparison of the resulting galvanometer deflection with that above noted gave at once an accurate measurement of the (magnetic or natural) rotation for any chosen wave-length. It should be noted that while this was the general method the procedure had to be varied somewhat for rotations as large as those encountered in quartz.

Sources of error incidental to the bolometric method have been discussed at some length in the previous articles and only some special precautions need be mentioned here.

A large (9 cm. high) 45° prism of dense glass gave somewhat higher dispersion than that used in most of the writer's previous experiments, although energy requirements preclude very great advances along this line. A test was made in the case of quartz of the errors due to slit and

bolometer widths by exaggerating the effect; the conclusion reached was that the maximum error from this cause did not exceed ½ per cent. The wave-length scale of the prism had originally been determined by double dispersion and comparison with rock salt. Repeated careful checks of the position of a number of infra-red solar absorption lines indicated that the probable error in the wave-length scale should be less than .01μ.

To eliminate a variety of errors, each measurement was preceded by a blank run with the cell or crystal in position *C* where it should, of course, produce no deflection, any effect shown here was applied as a small correction. Some precautions had to be used in this connection, particularly in the case of quartz, because of the slight polarizing action of the glass prism of the spectrometer. On the magnetic side careful tests for spurious rotations indicated that these did not in any case exceed 0.0006°.

Perhaps the best indication of the general accuracy of the results comes from the comparison which was made in several cases of the rotation measured bolometrically for the wave-length of the *D* lines with the same rotation measured with sodium light by the customary visual method using a tri-field polarizer. The agreement in every case was within 1 per cent.

RESULTS.

Six representative substances were tested, including a crystal, two organic liquids, two aqueous and one alcohol solution. One of the

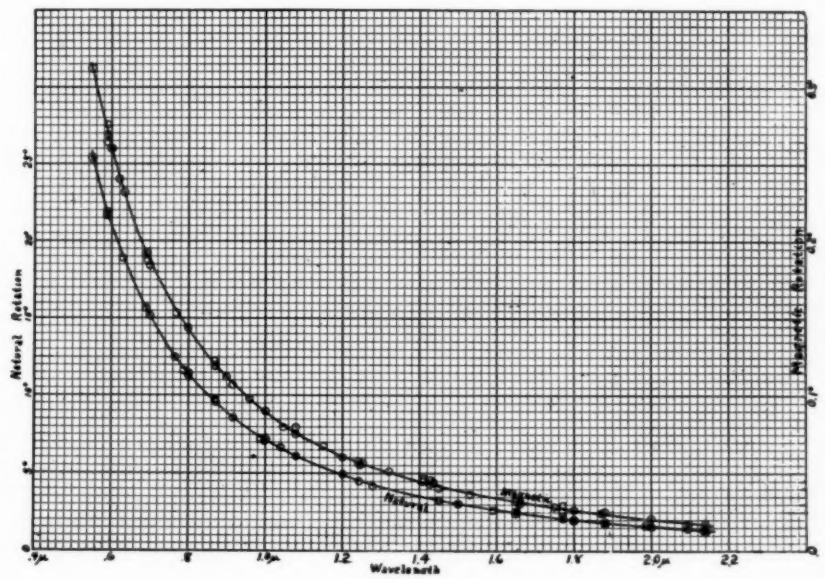

Fig. 3.

Rotary Dispersion Curves for Quartz.

solutions (tartaric acid) shows anomalous rotatory dispersion in the visible spectrum.

Quartz.

The sample tested was a clear piece of right-handed quartz 5.030 mm. thick. The rotation for the *D* line and 20° C. was found to be 21.739° per mm., in excellent agreement with the value of 21.728° found by Lowry. The actual measurements are plotted in Fig. 3 and are seen to lie with few exceptions very well on the curve. The tabulated values were read from the smooth curve (plotted on a large scale).

TABLE I.

Quartz—Rotation per Mm. at 20° C.

Wave-length, μ	Natural Rotation.					Magnetic Rotation, Observed.	Mag. R / Nat. R'
	Observed.		Calculated.		Temp. Coeff.		
	Present Work.	Others.	Lowry For-mula.	Gumlich For-mula.			
.5495	25.403°		25.201°			0.3120°	0.0123
.5893	21.739	21.728° (Lowry)	21.728	21.719°	.000164	.2694	.0124
.600	20.914		20.915		(39°−129° C.)	.2595	.0124
.700	15.139		15.124			.1860	.0123
.800	11.432		11.443		.000185	.1425	.0125
.900	8.873		8.953		(21°−141° C.)	.1119	.0126
1.00	7.121		7.189		.000152	.0890	.0125
1.08	6.123	6.18 (Carvallo)	6.122	6.20	(20°−141° C.)	.0752	.0123
1.10	5.904		5.893			.0724	.0123
1.20	4.918		4.911			.0603	.0123
1.30	4.101		4.151			.0516	.0126
1.40	3.515		3.549			.0448	.0127
1.45	3.272	3.43 (Carvallo)	3.295	3.41		.0418	.0128
1.50	3.030		3.055		.000156	.0389	.0128
1.60	2.662		2.669		(20°−125° C.)	.0341	.0128
1.70	2.348		2.341			.0303	.0129
1.715	2.304	1.83 (Moreau)	——			——	——
1.77	2.153	2.28 (Carvallo)	2.144	2.28		.0277	.0129
1.80	2.070		2.035		.000166	.0266	.0128
1.82	2.020	2.22 (Dongier)	2.017	2.15	(20°−113° C.)	.0259	.0128
1.90	1.827		1.835			.0234	.0128
2.00	1.614		1.636			.0205	.0127
2.10	1.431		1.466			.0179	.0125
2.14	1.372	1.60 (Carvallo)	1.404	1.55		.0169	.0123

Dispersion Formulæ.—Of the numerous formulæ which have been suggested to represent the natural rotatory dispersion of quartz we shall consider only two. The one used by Gumlich[1] is of the type

$$R = \frac{A}{\lambda^2} + \frac{B}{\lambda^4} + \cdots$$

to five terms. These five constants naturally permit a close fitting of calculated to experimental results and this Gumlich has done, using his own results in the visible spectrum, Soret and Sarasin's for the ultra-violet and Carvallo's and Dongier's infra-red observations quoted in Table I., in determining the constants.

Lowry[2] finds that the formula

$$R = \frac{11.6064}{\lambda^2 - \lambda_1^2} + \frac{13.42}{\lambda^2 - \lambda_2^2} - \frac{4.3685}{\lambda^2},$$

where

$$\lambda_1^2 = 0.010627; \quad \lambda_2^2 = 78.22,$$

λ being expressed in microns, represents his measurements in the visible spectrum with great accuracy. Using this formula *without changing the constants* in any way, the figures in Table I. were calculated. It will be noted that the agreement with the writer's observed values is exceedingly good throughout the range of the spectrum, the average divergence indeed being only a fraction of a per cent.

Wiedemann's Law.—Magnetic rotations for a field of approximately 9,400 gausses were made with the quartz in the same position as for the naturally active work. The ratios in Table I. show some variation, it is true, but part of this, at any rate, may be accounted for by the fact that the magnetic rotations were small and the probable error consequently larger than for the other rotations. There is certainly no consistent variation with wave-length and on the whole the results point strongly to the validity of Wiedemann's law for quartz over the whole spectral range investigated.

Temperature Coefficients.—The experimental arrangements for determining temperature coefficients of rotation were somewhat simpler than perhaps would have been the case if this had been the primary object of the investigation. The quartz was mounted in a simple brass cell, heated by a winding of resistance wire, the temperature being determined with a mercury thermometer. The results in Table I. vary somewhat but show no definite relation between coefficient and wave-length. Their mean value is in agreement with Gumlich's determination of 0.000165

[1] Loc. cit., p. 350.
[2] Loc. cit., p. 287.

(0°–100° C.) for the visible spectrum. Because of the very small changes involved the coefficient of magnetic rotation proved very hard to determine with any accuracy. The figures obtained, however, indicate a value somewhat higher than for the natural rotation.

Organic Liquids.

Liquids were tested in a cell 36 mm. diameter and 9.54 mm. thick, formed by drilling a hole through a plate of glass of this thickness. The sides were of thin plate glass which had been optically tested for strains. While they had no effect on the natural rotation as measured, correction had to be made, of course, for their magnetic rotation. It may be of interest to note that ordinary finely sifted Portland cement proved the most suitable substance for fastening the parts of the glass cell together. When adjoining surfaces were ground to give a good adhesion to the cement these cells proved entirely satisfactory for all the liquids and solutions tested.

Limonene and pinene were the organic liquids selected for test. The (dextro[1]) limonene was furnished through the kindness of Professor Kremers and Dr. Wakeman, of the pharmacy department, to both of whom the writer has been greatly indebted during the course of this investigation. Its density at 20° C. was .845 and boiling point 175° C. The $(d - \alpha)$ pinene was kindly furnished by Dr. Schorger, of the Forest Products Laboratory. It was distilled from Port Orford cedar, boiling point 155° C., density at 15° C. .863, and it had one of the highest recorded rotations for this substance. It was redistilled the day before testing.

The results are shown in Table II., the natural and magnetic rotations having been read from the smooth curves. The ratios of the two show no consistent variation with wave-length, indicating that Wiedemann's law holds as well for these liquids as for quartz. It is of interest to note in this connection, however, that the temperature coefficients for the two rotations may be quite different as shown by the results on limonene. This difference is exaggerated if the coefficients of specific rotation are calculated, taking account of the change in density with temperature; the specific natural rotation coefficient of this substance averages .0012 with the magnetic less than one fourth as much. Both show much greater and more irregular variations with wave-length.

The specific natural rotations listed in Table II. are expressed in the usual way in terms of a decimeter thickness and unit density.

[1] It is to be noted that what the chemist calls a dextro rotation is really a left-handed twist when viewed from the customary standpoint of the physicist, *i. e.*, along the path of the light. Thus right-handed quartz and dextro limonene really rotate in opposite directions.

TABLE II.

Optical Rotation of Two Terpenes at 22° C.

Wave-length, μ.	Limonene.						Pinene.			
	Observed Natural Rotation.	Temp. Coeff. (25°–120° C.) Nat. R.	Specific Rotation.	Observed Magnetic Rotation.	Temp. Coeff. (25°–120° C.) Mag. R.	Mag. R / Nat. R.	Observed Natural Rotation.	Specific Rotation.	Observed Magnetic Rotation.	Mag. R / Nat. R.
.50	13.915°		173.0°	3.571°		.257	5.716°	69.90°	3.252°	.569
.5893	9.665		120.1	2.475		.256	3.968	48.48	2.291	.577
.60	9.220		114.6	2.363		.257	3.818	46.59	2.196	.575
.70	6.482	−.00201	80.56	1.639	−.00114	.253	2.708	33.09	1.463	.540
.80	4.950	−.00206	61.55	1.229		.248	2.066	25.24	1.119	.541
.90	3.825		47.54	0.938		.245	1.606	19.61	0.870	.542
1.00	3.024	−.00205	37.61	0.747	−.00114	.247	1.286	15.71	0.702	.546
1.10	2.500		31.09	0.622		.249	1.058	12.93	0.573	.542
1.20	2.059	−.00201	25.60	0.522		.253	0.876	10.73	0.495	.564
1.30	1.734		21.57	0.445		.257	0.742	9.06	0.433	.584
1.40	1.509		18.76	0.383		.254	0.640	7.82	0.365	.570
1.50	1.325	−.00192	16.48	0.342	−.00117	.258	0.542	6.62	0.303	.560
1.60	1.191	−.00192	14.81	0.308	−.00123	.259	0.500	6.11	0.273	.547
1.90	0.870		10.82	0.232		.266	0.408	4.99	0.232	.567
2.00	0.780		9.70	0.208		.267	0.380	4.64	0.222	.583

Absorption Bands.—Both limonene and pinene show marked absorption bands at 1.2μ and 1.4μ while the extinction at 1.8μ is too great to allow of reliable measurements in this region. Theories of optical activity agree that absorption which is electronic in character may produce anomalies in the rotatory dispersion curve. Drude associates such anomalies only with those electrons which vibrate along spiral paths, but the recent theory proposed by Gray[1] and experimentally verified for solutions of neodymium nitrate, assumes that any absorption band belonging to an electron in an active molecule may be accompanied by an anomaly.

The fact that limonene and pinene show no such anomalies may, however, be explained in several ways. The dispersion may not have been great enough to detect them, although this is considered unlikely as the bolometer subtended less than .02μ in this part of the spectrum. A more reasonable assumption is that these absorption bands are not primarily electronic in their origin and hence would not be expected to be accompanied by anomalies in dispersion.

[1] Frank Gray, PHYS. REV., 7, p. 472 (1916).

Solutions.

Three solutions were experimented with: a 20 per cent. (by weight) aqueous solution of cane sugar (density at 22° C., 1.081); a 28.62 per cent. aq. solution of tartaric acid (density at 22° C., 1.140); and a 34.70 per cent. solution of camphor in absolute alcohol (density at 20° C., 0.845). The last two were chosen because they (*i. e.*, same percentage solutions) had been previously examined by Nutting[1] in his study of ultra-violet rotatory dispersion. All show dextro-rotations in the spectral region examined in the present work.

The results are shown in Table III. The specific rotations (*i. e.*,

TABLE III.

Optical Rotation of Three Solutions.

Wave-length. μ.	Tartaric Acid (20° C.).			Cane Sugar (22° C.).			Camphor (20° C.).		
	Observed Natural Rotation.	Specific Rotation.	Mag. R / Nat. R'	Observed Natural Rotation.	Specific Rotation.	Mag. R / Nat. R'	Observed Natural Rotation.	Specific Rotation.	Mag. R / Nat. R'
.45	0.365°	11.71°	——	——	——	——	——	——	——
.50	0.387	12.42	——	——	——	——	——	——	——
.55	0.369	11.84	——	——	——	——	——	——	——
.60	0.318	10.21	5.75	1.288°	62.48°	1.42	1.098°	39.26°	1.51
.70	0.227	7.28	5.68	0.922	44.68	1.40	0.725	25.92	1.64
.80	0.181	5.80	5.51	0.700	33.93	1.42	0.528	18.87	1.71
.90	0.147	4.71	5.34	0.543	26.32	1.44	0.388	13.87	1.75
1.00	0.118	3.78	5.34	0.428	20.76	1.47	0.308	11.01	1.80
1.10	0.098	3.15	5.31	0.351	17.02	1.48	0.245	8.75	1.89
1.20	0.082	2.63	5.25	0.293	14.21	1.55	0.194	6.93	2.13
1.30	0.067	2.15	——	0.246	11.93	1.52	0.164	5.86	2.16
1.40	——	——	——	——	——	——	0.145	5.18	2.17

the rotations per decimeter divided by the product of the density and percent (by weight) strength of solution) for tartaric acid and cane sugar are in good agreement with the values listed by Landolt in his *Optische Drehungsvermögen*, but the camphor is somewhat low. The curve of the natural rotatory dispersion of tartaric acid is shown in Fig. 4. The other curves are of the same general character as those for limonene or quartz and show no anomalies. Tartaric acid has long been known to exhibit anomalous rotatory dispersion and Nutting found that in solutions of this concentration the rotation changes sign at $\lambda = .38\mu$ and becomes negative for shorter wave-lengths and with much larger values. The interesting point about this curve in Fig. 4 is that the

[1] P. G. Nutting, PHYS. REV., 17, p. 1 (1903).

anomalous character disappears entirely after $\lambda = .6\mu$ and the dispersion is quite similar to that of the other substances for longer wave-lengths.

The ratio of magnetic and natural rotations is seen to be less constant for these solutions than for the former substances. Camphor shows the greatest variation from Wiedemann's law, although tartaric acid would unquestionably prove a striking exception for wave-lengths shorter

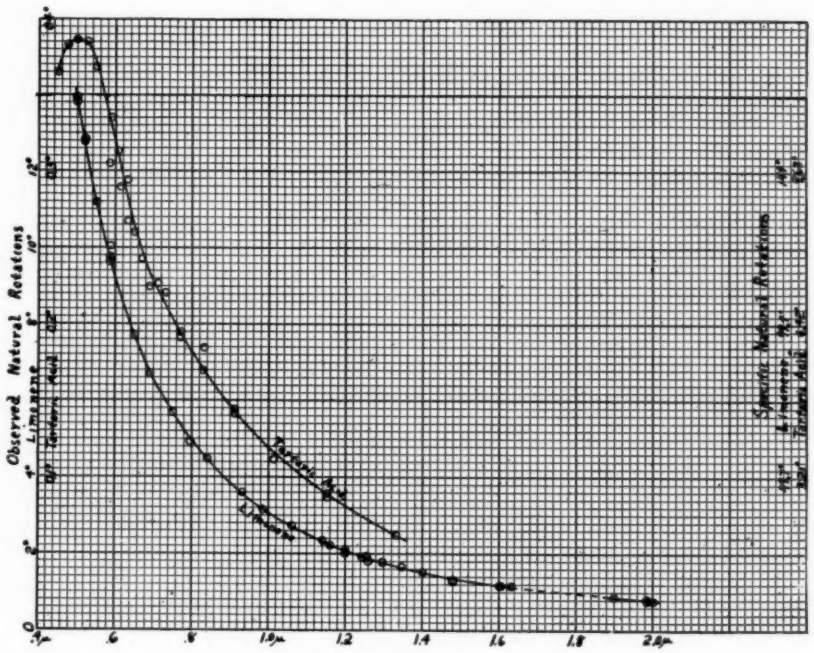

Fig. 4.

Rotatory Dispersion Curves for Limonene and Tartaric Acid.

than .6μ had the magnetic rotation been investigated in this region. These shorter wave-length points were obtained by visual measurements with a 20 cm. tube which did not lend itself readily to magnetic investigations. The magnetic rotatory dispersion of both tartaric acid and cane sugar solutions in the spectral region investigated is, however, practically identical with that of pure water and may be safely assumed to be such in this region also. In discussing Wiedemann's law for solutions some writers (vide Darmois, loc. cit.) attempt to separate the magnetic rotations of the solvent and solution, but the writer is sceptical of the value of such calculations and has not made use of them here.

Dispersion Ratios.—The relative dispersions of the various substances tested may be seen at a glance from the following table in which the

rotation for wave-length .6μ is called unity in each case. It will be noted that in practically all cases the rotations decrease in value more rapidly than the inverse square of the wave-length.

TABLE IV.

Wave-length, μ.	Inverse Square.	Quartz.		Limonene.		Pinene.		Cane Sugar.		Tartaric Acid.		Camphor.	
		Nat. *R.*	Mag. *R.*	Nat. *R.*	Mag. *R.*	Nat. *R.*	Mag. *R.*	Nat. *R.*	Mag. *R.*	Nat. *R.*	Mag. *R.*	Nat. *R.*	Mag. *R.*
.60	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
.80	0.563	0.547	0.549	0.537	0.520	0.541	0.510	0.544	0.543	0.569	0.543	0.481	0.547
1.00	0.360	0.340	0.343	0.328	0.316	0.337	0.320	0.333	0.344	0.371	0.344	0.281	0.335
1.30	0.213	0 196	0.199	0.188	0.188	0.194	0.197	0.191	0.204	0.211	——	0.149	0.213
1.60	0.141	0.127	0.131	0.129	0.130	0.131	0.124	——	——	——	——	——	——
2.00	0.090	0.077	0.079	0.084	0.088	0.099	0.101	——	——	——	——	——	——

In conclusion the writer takes pleasure in acknowledging his indebtedness to the Rumford Fund. A large share of the apparatus with which these measurements were carried out was originally purchased with grants from this source.

SUMMARY.

1. The natural and magnetic rotatory dispersions of quartz, limonene, pinene, and solutions of cane sugar, tartaric acid and camphor have been determined over a range of wave-lengths from the visible to beyond 2μ. The curves are all regular save in the case of tartaric acid in the shorter wave-lengths.

2. The natural rotation for quartz over the whole spectral range agrees very well with the formula used by Lowry, with constants determined by him from visible spectrum observations.

3. The temperature coefficients of rotation as determined for quartz and limonene show no definite dependence on wave-length. The natural and magnetic rotation coefficients have quite different values, however, in the case of limonene.

4. Wiedemann's law of the proportionality of natural and magnetic rotations holds with a fair degree of approximation for quartz and the two terpenes over the whole spectral range investigated. It does not hold as well for the solutions, the variation being greatest in the case of camphor.

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THEORETICAL CONSIDERATIONS ON THE NATURE OF METALLIC RESISTANCE, WITH ESPECIAL REGARD TO THE PRESSURE EFFECTS.

BY P. W. BRIDGMAN.

IN a recent number of the Proceedings of the American Academy[1] I have given data for the effect of pressures to 12,000 kg. and temperatures between 0° and 100° C. on the electrical resistance of 22 metals. A detailed discussion of the nature of the results and methods of measurement and calculation will be found in that paper. The most important results follow. (1) The temperature coefficient of resistance is nearly independent of pressure; this holds for pressures high enough to compress the metal in many cases to less than its volume at 0° Abs. Another way of stating the same fact is that the pressure coefficient is independent of temperature. (2) The relative pressure coefficient of resistance becomes less at higher pressures. (3) The curvature of the resistance-pressure curves is in most cases greater at lower temperatures. (4) Two metals, bismuth and antimony, show an abnormal positive pressure coefficient of resistance. The anomaly of bismuth was known before, but that of antimony is new.

The purpose of this paper is to present a view of the nature of metallic conduction which had its origin in an attempt to bring into line the facts at high pressures, but which also accounts for other facts not intimately connected with the pressure effects. In brief, this view of the nature of conduction regards all metals as naturally perfect conductors in the sense that the electrons may pass without resistance from atom to atom when the atoms are in contact at rest. The precise mechanism of this free transfer need not be further specified for our purposes; we may if we like suppose the electrons capable of freely penetrating the substance of the atom, in much the same way as recently suggested by Professor Hall.[2] If the atoms become too much separated, however, the electrons encounter difficulty in passing from atom to atom, and if the separation is too great, are almost entirely unable to pass. In a solid at absolute zero the electrons pass freely from atom to atom, thus giving perfect conductivity, but as the temperature is raised, the atomic centers become separated, and if the separation passes a certain critical value, the electrons encounter

[1] P. W. Bridgman, Proc. Amer. Acad., 52, 571–646, 1917.

[2] E. H. Hall, Proc. Amer. Acad., 50, 67–103, 1914.

difficulty, and electrical resistance makes its appearance. In a solid under given conditions there must be a certain number of pairs of atoms separated by more than the critical distance, or we may say, there are a certain number of "gaps." The resistance is proportional to the number of gaps. Now the number of gaps evidently is closely connected with the mean amplitude of oscillation of the atoms. Our first task, in attempting to cast this view of the nature of conduction into quantitative form, is to find how the amplitude changes with pressure and temperature.

The following deduction of the variation of amplitude and frequency is valid only at moderate temperatures, where the classical statistical mechanics and quantum theory are not essentially in conflict. For these temperatures, everything may be obtained from three equations. We assume in the first place that the vibration of an atom is simple harmonic, and that the energy of a degree of freedom is equal to the energy of a degree of freedom of a gas atom at the same temperature. This gives as a first equation

$$\nu^2\alpha^2 = \text{const } \tau, \tag{1}$$

where ν is the average frequency of atomic vibration, and α is the average amplitude. The second assumption concerns the nature of the restoring force under which the atoms execute their harmonic vibrations. If the volume remains unaltered, it is natural to suppose that in most cases the average restoring force for a given displacement will not be affected by such changes as changes of temperature. We therefore write as the second equation

$$\left(\frac{\partial \nu}{\partial \tau}\right)_v = 0. \tag{2}$$

These two relations are not enough to completely determine ν and α as functions of pressure and temperature. As the third equation I will adopt Grüneisen's relation[1]

$$\frac{1}{\nu}\left(\frac{\partial \nu}{\partial p}\right)_\tau = \frac{1}{C_p}\left(\frac{d v}{\partial \tau}\right)_p. \tag{3}$$

These three relations must all be recognized as only approximate. At low temperatures $\nu^2\alpha^2$ increases more rapidly than τ, and at high temperatures there may be further increase. The frequency cannot be a function of volume only unless at constant volume the average restoring force on an atom is a linear function of atomic displacement. But it seems inevitable that as the amplitude of oscillation becomes greater the restoring force, due to contact between atoms, must increase more

[1] E. Grüneisen, Ann. Phys., 39, formula 23, p. 276, 1912.

rapidly than the displacement, resulting in an increase of frequency as temperature is increased at constant volume. The existence of an effect of this nature is demonstrated by the existence of a positive thermal expansion. For if the restoring force were truly linear, the expansion must probably vanish, as I have suggested in connection with effects found in liquids at high pressures, and as Debye[1] has suggested more recently. Equation (2) is, therefore, only a first approximation. Grüneisen's relation, equation (3), is in accordance with an equation of quantum theory, obtained by assuming Planck's relation between energy and entropy. Planck finds that the entropy is a determinate universal function of ν/τ. Grüneisen's assumption is more general than the relation obtained from quantum theory, in that he assumes entropy a function only of ν/τ without assuming anything at all about the special form of the function; in fact he does not even assume that the function is of the same form for different substances. Since the particular form of the function demanded by quantum theory seems to suit the facts at atmospheric pressure fairly well, we are reasonably safe in assuming Grüneisen's less restricted form.

From equations (2) and (3) above we obtain immediately $(\partial\nu/\partial p)_\tau$ and $(\partial\nu/\partial\tau)_p$. These are the derivatives which we want, because in this work p and τ are taken as the independent variables. We have, from (2)

$$\left(\frac{\partial\nu}{\partial\tau}\right)_v \equiv \left(\frac{\partial\nu}{\partial\tau}\right)_p + \left(\frac{\partial\nu}{\partial p}\right)_\tau \left(\frac{\partial p}{\partial\tau}\right)_v = 0,$$

and from (3)

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_s \equiv \frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_\tau + \frac{1}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p \left(\frac{\partial\tau}{\partial p}\right)_s = 0.$$

But

$$\left(\frac{\partial p}{\partial\tau}\right)_v = -\left(\frac{\partial v}{\partial\tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau, \quad \text{and} \quad \left(\frac{\partial\tau}{\partial p}\right)_s = \frac{\tau}{C_p}\left(\frac{\partial v}{\partial\tau}\right)_p.$$

Substituting and solving, we obtain

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p = \left(\frac{\partial v}{\partial\tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau, \tag{4}$$

and

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_\tau = \left(\frac{\partial v}{\partial\tau}\right)_p \Big/ C_v. \tag{5}$$

Now differentiating (1) logarithmically, and eliminating $(1/\nu)(\partial\nu/\partial\tau)_p$ and $1/\nu)(\partial\nu/\partial p)_\tau$ we have immediately

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau = -\left(\frac{\partial v}{\partial\tau}\right)_p \Big/ C_v, \tag{6}$$

[1] P. Debye, Wolfskehl. Conference, Göttingen, 1914, p. 19–60.

and

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{1}{2\tau} - \left(\frac{\partial v}{\partial\tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau . \tag{7}$$

These equations give, therefore, the variation of both ν and α in any direction in terms only of quantities of thermodynamic nature.

The numerical magnitudes of these quantities first claim attention. The relative pressure coefficient of amplitude is negative, and its magnitude is in general six to nine times the linear compressibility. The amplitude increases with increasing temperature, approximately as $1/2\tau$, since the term $(\partial v/\partial\tau)_p^2/(C_v(\partial v/\partial p)_\tau)$ is small. The frequency increases with increasing pressure, the rate of increase being the same as the rate of decrease of the amplitude, and the frequency decreases with increasing temperature, but the rate of decrease is small compared with the rate of increase of amplitude.

TABLE I.

Metal.	$-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$.	$\frac{1}{v}\left(\frac{\partial v}{\partial\tau}\right)_p$.	C_v Kg. Cm. per Cm³.	$\frac{1}{a}\left(\frac{\partial a}{\partial\tau}\right)_p$.	$-\frac{1}{a}\left(\frac{\partial a}{\partial p}\right)_\tau$.	$-\frac{1}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p$.
In.....	(?)2.0×10⁻⁶	.0₃13	15.2	2.39×10⁻³	8.6×10⁻⁶	55.5×10⁻⁶
Sn.....	1.86	.0₄51	16.8	1.92	3.03	8.3
Tl.....	2.26	.0₄92	15.4	2.06	5.96	24.3
Cd.....	2.06	.0₄90	19.2	2.04	4.7	20.4
Pb.....	2.28	.0₄879	14.0	2.07	6.27	24.3
Zn.....	1.66	.0₄78	26.8	1.97	2.91	13.7
Mg.....	2.84	.0₄78	17.7	1.96	4.4	12.1
Al.....	1.44	.0₄74	23.1	2.00	3.19	16.5
Ag.....	.99	.0₄55	24.1	1.96	2.30	12.9
Au.....	.628	.0₄429	24.8	1.95	1.73	11.8
Cu.....	.735	.0₄51	34.2	1.94	1.49	10.3
Ni.....	.42	.0₄375	40.0	1.88	.94	8.4
Co.....	? .50	.0₄37	37.0	1.91	1.00	7.5
Fe.....	.58	.0₄375	34.6	1.90	1.08	7.0
Pd.....	.53	.0₄355	29.4	1.92	1.21	8.1
Pt.....	.272	.0₄292	28.5	1.94	1.02	10.9
Mo.....	.45	.0₄108	24.7	1.84	.44	1.13
Ta.....	.52	.0₄237	22.8	1.88	1.04	4.85
W.....	.265	.0₄101	27.6	1.84	.37	1.39

In Table I. are collected the numerical values of the changes of amplitude and frequency for the metals whose pressure coefficient I have measured. In the table are also included the fundamental thermodynamic data used in the calculations. There is often considerable uncertainty as to the best experimental values to choose. I have in general used for thermal expansion the most consistent values from the last edition of Landolt and Börnstein and for compressibility the values of

Richards. A more detailed discussion of the manner of choice of these data may be found in the American Academy paper.

With the numerical values of the changes of amplitude at hand, we are now in a position to search for a connection between the changes of resistance and amplitude. It turns out that there is a very simple approximate relation between these two quantities, which I offer as the most important result of this paper. The relation is that the change of resistance with temperature or pressure or any other thermodynamic variable is twice the relative change of amplitude under the same conditions. It is perhaps worth mentioning that I was led to search for a relation between resistance and amplitude by the view I have outlined of the nature of resistance, and that the view was not suggested by observing the relation.

Consider first the variation of resistance with temperature. In order to simplify this first discussion, we consider the temperature coefficient at constant volume, thus avoiding a very small correction for changing volume. From the formulas already given, it follows immediately that

$$2\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_v = \frac{1}{\tau}.$$

Now the temperature coefficient of most metals is nearly the reciprocal of the absolute temperature, so that we have here an approximate expression for the change of resistance in terms of the change of amplitude. The temperature coefficient as ordinarily given, however, is the coefficient of the observed resistance at constant pressure. The coefficient at constant volume is more nearly equal to $1/\tau$ than is the coefficient at constant pressure. In Table II. are shown the temperature coefficients at constant volume of the specific resistance at 0° C. In comparing these values with others it must be remembered that we are giving here the specific resistance, and not the observed resistance, and also that we are listing the instantaneous coefficient at 0° and not the average coefficient between 0° and 100°.

The temperature coefficient at constant pressure involves a correction for changing volume, as already suggested. If the view of conduction given above is justified, we would expect that decreasing the number of atoms would, other things being equal, increase the resistance. The increase is proportional to the change of linear dimensions, that is to $\frac{1}{3}(1/v)(\partial v/\partial\tau)_p$, because an increase of length and an increase of one of the cross sectional dimensions work in opposite directions on the resistance. It turns out that to the same degree of approximation to which $(1/w)(\partial w/\partial\tau)_v$ is equal to $2(1/\alpha)(\partial\alpha/\partial\tau)_v$, $1/w(\partial w/\partial\tau)_p$ is also equal to

$2(1/\alpha)(\partial\alpha/\partial\tau)_p + \frac{1}{3}(1/v)(\partial v/\partial\tau)_p$. It is hardly worth while to give a special table for this other temperature coefficient. The correction for volume averages about $\frac{1}{2}$ per cent.

TABLE II.

Metal.	$\frac{1}{w}\left(\frac{\partial w}{\partial \tau}\right)_v$.	$\gamma \equiv \frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau$.		Ratio of γ calc. by Grüneisen's Formula to γ Obs.	$\frac{\left(\frac{\partial \tau}{\partial p}\right)_w}{\left(\frac{\partial \tau}{\partial p}\right)_\alpha}$.
		$\gamma_{Obs.}$	$\frac{\gamma_{Calc.}}{\gamma_{Obs.}}$.		
In.....	.00360	-12.9×10^{-6}	1.39	1.063	0.875
Sn.....	402	11.1	0.597	0.420	1.62
Tl.....	463	13.9	0.91	0.813	0.932
Cd.....	357	11.3	0.894	0.643	1.21
Pb.....	350	15.2	0.875	0.671	1.23
Zn.....	389	5.95	1.066	0.718	0.99
Mg.....	380	6.4	1.547	1.094	0.72
Al.....	409	4.64	1.48	1.157	0.665
Ag.....	384	3.83	1.288	0.973	0.800
Au.....	369	3.33	1.132	0.877	0.949
Cu.....	414	2.45	1.315	0.985	0.738
Ni.....	605	1.72	1.09	1.197	0.568
Co.....	358	1.10	1.975	1.328	0.573
Fe.....	545	2.60	0.905	0.807	0.815
Pd.....	308	2.16	1.205	0.792	1.057
Pt.....	367	2.07	1.030	0.865	1.007
Mo.....	432	1.48	0.601	0.338	1.443
Ta.....	290	1.66	1.356	0.814	1.007
W.....	313	1.37	0.598	0.305	1.354

We next compare the pressure coefficient of resistance at constant temperature with the change of amplitude with pressure at constant temperature, corrected for the effect of changing volume as just explained. The pressure coefficient computed in this way is given by the formula

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau = 2\,\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\tau + \tfrac{1}{3}\,\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau.$$

The last term, which is the correction factor for changing volume, amounts to from 5 to 10 per cent. of the total effect. In Table II., Column 4, the ratio of the observed value of the pressure coefficient of specific resistance at 0° C. and 0 kg. to the value computed as above is shown.

The agreement is not as good as could be desired, but it should be remembered that the classical free electron theory did not give even the right sign to the pressure effect, to say nothing of the numerical magnitude, and that there has been only one other theory proposed which has

attempted to account for the pressure effect. This other theory is that of Grüneisen,[1] who modifies the theory of Wien,[2] who regards the electrons as moving with constant velocities independent of the temperature. The formula of Grüneisen is

$$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau = \frac{1}{u}\left(\frac{\partial u}{\partial p}\right)_\theta - \frac{1}{N}\left(\frac{\partial N}{dp}\right)_\theta - \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\theta - \frac{1}{C_p}\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p\left[1 + \frac{1}{w}\left(\frac{\partial w}{\partial \tau}\right)_p{}^\tau\right],$$

where u is the velocity of the free electrons, and N is their number per cm^3. In column 5 of Table II. the ratio of the values computed by Grüneisen's formula to the observed values are listed for purposes of comparison. It will be seen that on the whole the new formula agrees better with experiment than does that of Grüneisen. Grüneisen has discrepancies amounting to a factor of three for both Mo and W, whereas the greatest discrepancy of the new formula is by a factor of two for Co, which was known to be impure. There is also this difference between the new formula and that of Grüneisen, apart from its much greater simplicity. Grüneisen's formula does not give the pressure coefficient in terms only of other quantities of non-electrical nature, but, besides the first two terms which are small, introduces the temperature coefficient of resistance, which must be determined by experiment. It is of course true that the temperature coefficient is approximately equal to $1/\tau$, so that the last factor in Grüneisen's formula might have been written 2, but the formula would then have lost its theoretical significance, and become merely empirical. Furthermore, the agreement with observation would not have been so good if this simplification had been made, the departures of the temperature coefficients from equality with $1/\tau$ playing a real part in the numerical values given by the formula.

It is interesting to notice that by a combination of Grüneisen's formula with that suggested above, an empirical relation may be obtained much better than either. The relation is

$$\gamma_G/\gamma_{Obs} + \gamma_{Obs}/\gamma_B = \text{Const.}$$

where $\gamma = (1/w)(\partial w/\partial p)_\tau$ and the subscripts indicate whether the coefficient is observed or calculated according to Grüneisen's or my formula. The "constant" varies for the 19 normal metals from 1.54 to 1.97, or a range of 14 per cent. about the mean, whereas the variation in Grüneisen's formula, omitting Co, is 53 per cent., and that of the proposed formula above, omitting Co, is 37 per cent. It is curious, however, that the formula cannot be reversed, that is solved for γ_{Obs} to give an approxi-

[1] E. Grüneisen, Verh. D. Phys. Ges., 15, 186–200, 1913.

[2] W. Wien, Columbia Lectures, 1913, 29–48.

mately correct value. It will be found, if one tries to operate with a fixed average value of the constant, that some substances give imaginary values for γ_{Obs}.

A result of some interest to be deduced from the expressions above for temperature and pressure coefficient is that the resistance is approximately constant along a line of constant amplitude. Column 6 in Table II. shows the ratio of $(\partial\tau/\partial p)_w$ to $(\partial\tau/\partial p)_\alpha$. This ratio of course should be unity if resistance were strictly constant at constant amplitude.

We may summarize the results of these numerical calculations by the statement that the change of specific resistance with either pressure or temperature, and therefore with any other thermodynamic variable, is given by

$$\frac{1}{w}dw = 2\frac{1}{\alpha}d\alpha + \tfrac{1}{3}dv,$$

to at least as good a degree of approximation as that of any other formula. The term containing the change of volume is comparatively unimportant, so that we may say that *the relative change of specific resistance in any direction is approximately equal to twice the corresponding change of average amplitude of atomic vibration.* The agreement with the pressure coefficient is better than that of the only previously proposed formula, and the temperature coefficient is correctly reproduced in the majority of cases. I know of no attempt to account for the departures of the temperature coefficient from $1/\tau$ except that of Wien, and his attempt to bring the departures into connection with the average frequency of atomic vibration cannot be considered a success.

The theoretical significance of this general relation becomes immediately obvious from the viewpoint outlined above that the resistance is proportional to the number of gaps between atoms. If the number of gaps is proportional to the square of the mean amplitude, then the change in the relative resistance will be proportional to twice the relative change of mean amplitude, plus a correction term for changing volume. Now it is easy to see how the number of gaps may be proportional to the square of the mean amplitude. A gap is formed when two neighboring atoms each have an amplitude enough greater than the mean so that the maximum distance of separation, when they are at opposite parts of their swing, shall exceed a critical value. That is, a gap is only produced by the chance coincidence in two neighboring atoms of two amplitudes both larger than the mean. If we suppose the amplitudes are distributed at random, the chance that there be two such coincident large amplitudes in two neighboring atoms is evidently proportional to the square of the chance that a single atom have an amplitude large enough. If then, the

chance that a single atom have an amplitude of the requisite magnitude be proportional to the mean amplitude of oscillation of all the atoms, and this is certainly the simplest assumption that can be made, the connection becomes at once obvious. Of course in any actual case the conditions are much more complicated than we have supposed above; the amplitude of a single atom need not exceed a definite critical value before it can under any conditions form a gap with a neighboring atom, but the amplitude necessary to form a gap will depend on the relative phases of the two atoms. Such modifying features as this will not change the general result that the number of gaps is proportional to the square of the number of atoms with amplitude above a certain value, but will only change the numerical value of the factor of proportionality.

It is evident that these general considerations must be modified by many factors that vary from substance to substance. Consider first the manner of distribution of amplitudes about the mean. This is a subject which has not yet been worked out, but which can perhaps be solved in the not too distant future by such methods as those initiated by Born[1] in his recent book. Whatever the precise manner of distribution will turn out to be, we may be sure that it will not be Maxwell's distribution. I have obtained independent evidence on this point from the time rate of transition of polymorphs.[2] If one does assume Maxwell's distribution, the variation of number of gaps with mean amplitude may be worked out, and will be found proportional to some higher power of the mean amplitude than the second. This is sufficient to show that the manner of variation of number of gaps depends on the manner of distribution of amplitudes about the mean. The manner of distribution may well be expected to vary from substance to substance.

It is obvious, if all amplitudes are concentrated in a narrow band about the mean, that as temperature is increased from 0° Abs. there will be a definite temperature at which a finite number of gaps will suddenly appear, and the metal will suddenly become conducting, as do tin, lead, and mercury. This suggestion as to the sudden appearance of resistance must not be taken too seriously at present until it has been settled that this discontinuity is not due to a polymorphic transition, but in any event the new point of view leaves open such a possibility. If, on the other hand, the distribution is not so sharp, the appearance of resistance will not be so sudden, but in any event it is pretty evident that the resistance will at first, after it has once appeared, increase more rapidly than the increase of temperature itself. This is of course true for most pure metals; at low temperatures the resistance increases approximately as the

[1] M. Born, Dynamik der Krystallgitter, Teubner, 1915.

[2] P. W. Bridgman, Proc. Amer. Acad., 52, 80, 1916.

fourth power of the temperature. The fact that the manner of variation of resistance with temperature is much the same for all metals at low temperatures suggests that at low temperatures, at least, the manner of distribution of amplitudes must be much the same for all substances. At higher temperatures individual differences in the behavior of resistance appear, and it seems not unlikely that similar differences in the manner of distribution should also appear.

Another important consideration is that of frequency. We have entirely neglected this factor in the considerations above. If frequency has no effect, then the effective number of gaps is not changed by a change of frequency. This means that if we double the frequency of oscillation we have thereby halved the time during which two atoms are separated by the critical distance during a single encounter, or doubling the rapidity of mean oscillation doubles the rapidity of every stage of the motion. This seems the most natural hypothesis, but judging by analogy with the collisions of elastic systems, it is by no means a necessary hypothesis. If the law of action between atoms is different for different kinds of atoms, there may be differences in the proportional length of time occupied in a collision. It does not seem unlikely that there should be such variations, and probably some of the discrepancies are to be explained by this neglected factor. The fact, however, that we have obtained as good agreement as we have probably means that the atoms of all normal metals are much alike. It ought to be possible to obtain information about the law of force between atoms by considerations of this character.

Perhaps the most striking factor that has been neglected is the effect of change of volume, apart from the effect on the number of atoms in unit volume. If the atoms are of finite size, and if this size remains constant, it is evident that when volume is decreased at constant amplitude, for example, the number of gaps and therefore the resistance should decrease. If the total volume occupied by the atoms is a large fraction of the total volume of the solid, such an effect should be rather large. According to Wien's theory, on the other hand, the resistance should increase instead of decrease as volume is decreased at constant amplitude. As a matter of fact, there seems to be no such effect; for some metals the resistance decreases with decreasing volume at constant amplitude, and for others the resistance increases. In any event the effect is small; in fact, to a first approximation, resistance is constant for all normal metals at constant amplitude, as has been shown in Table II. The point is an important one, and seems to me to indicate that under pressure the atom undergoes some sort of distortion so as to become effectively smaller. The same conclusion is strongly suggested by the fact that at pressures

high enough to compress the volume to less than its value at 0° Abs. the temperature coefficient is practically unaffected. This would seem to indicate that the solid in some way remains similar to itself as pressure is increased, and this might be brought about by such a decrease of volume of the atoms themselves as to keep pace with the change of volume of the entire solid.

Another possibility to be kept in mind is that the boundary of the atom which determines the elastic collisions may not be the same as the boundary which determines the gaps for the passage of electrons. The latter may be inside the former, much in the same way as the effective radius of the atom as determined from dielectric measurements has been found to be less than the effective radius as found from kinetic theory. In fact, this view of the nature of conduction demands fundamentally a certain amount of interpenetration of the outer parts of the fields of force surrounding the atoms when they are in contact under normal circumstances in a solid, or else a very considerable distortion of the atom under changes of temperature. Or again, the atoms may not be absolutely separated in order to form a gap, but may be merely in contact over a smaller area, thus affording less chance for the passage of electrons.

In view of all these neglected factors it does not seem strange that the variations from the formula are as large as they are, but rather that they are no larger. It must be one of the next tasks of this theory to attempt to bring the variations from agreement with the formula into connection with the neglected factors, and obtain if possible a closer approximation to the observed values.

This is as far as I have been able to get quantitatively according to this view point. Qualitatively, however, many other facts may be brought into line if we consider that at high temperatures the gaps begin to function in a new way. Consider a metal kept at constant volume as temperature increases. If the volume is initially small, the number of gaps will increase, as already explained, as the average amplitude of oscillation is increased. But if the initial volume is large, the atoms may be separated so far that the electrons cannot pass freely from atom to atom under ordinary conditions, but can pass only when two atoms are brought especially close together during a collision of unusual violence. The number of such favorable opportunities will evidently increase as the mean amplitude increases. An increase of amplitude functions in two ways, therefore; at small volumes it increases the resistance by increasing the number of gaps, and at large volumes it decreases the resistance. If the metal is heated at constant pressure, being allowed to expand, there will be a progression from the first state of affairs toward the second. We

may represent this by saying that effectively the atoms of the metal are divided into two classes; those of the first class are the ones to which we have already applied our formulas, and their resistance increases with increasing amplitude, while those of the second class tend to decrease in resistance as mean amplitude increases. The atoms of the first class have a low specific resistance, and those of the second class a high resistance. As the metal is heated the resistance will be affected in three ways; there will be an increase of resistance of the atoms of the first class, an increase of resistance due to the passage of atoms from the first to the second class, and a decrease of resistance of the atoms of the second class.

We now enumerate the various kinds of effect that can be brought into line by these considerations. This enumeration will include the facts that have already received quantitative treatment. (1) The temperature coefficient of resistance of solid metals at constant pressure is very nearly equal to $1/\tau$. It is, however, greater than $1/\tau$, and for nearly all metals becomes increasingly greater at higher temperatures. (2) The temperature coefficient of most liquid metals, on the other hand, is much less than $1/\tau$, and for some metals (Cd and Zn) may actually be negative. (3) The only liquid metal for which measurements have been made, mercury, has a negative temperature coefficient of resistance at constant volume. (4) At constant volume the temperature coefficient of solid metals becomes increasingly less than $1/\tau$ as temperature is raised, and if the same tendency persists will eventually become negative. (5) At very low temperatures some metals show a sudden drop of resistance to sensibly zero. (6) The pressure coefficient of resistance at constant temperature of nearly all pure metals is negative. The pressure coefficient of the only liquid metal measured, mercury, is much larger than that of solids. (7) The relative pressure coefficient at constant temperature decreases with increasing pressure. (8) The decrease with pressure of pressure coefficient at constant temperature is less at higher temperatures for most metals, but for a few metals with low melting point is greater. (9) If a metal is stretched by a force in tension, the resistance along the line of stretch is increased, but is decreased at right angles. (10) Two metals, Bi and Sb, have a positive pressure coefficient. This may be brought into direct connection with their abnormally small thermal expansion and the fact that both expand on freezing. (11) The high specific resistance of alloys compared with that of their constituents is what one would expect. The negative temperature coefficient of some alloys may also be explained by the same mechanism, and possibly the positive pressure coefficient.

We now consider these points in detail. (1) The temperature coef-

ficient of solid metals, both at constant pressure and constant volume has already been discussed. One would be tempted to explain the fact that the coefficient is greater than $1/\tau$ by the passage of atoms from the first to the second state on raising temperature, but this explanation is seen not to be justified on considering that the coefficient at constant volume is also too large, and that the discrepancy at constant pressure is no greater than at constant volume. An explanation of the variations of temperature coefficient is much to be desired; as yet there seems to be no suggestion as to any possible connection with other physical properties. As already remarked, Wien's attack does not seem fruitful. Possibly a suggestion may be found in a distortion of the atoms with increasing violence of vibration, even at constant volume, which effectively decreases their volume, and so increases the number of gaps and the resistance. The upward curvature of the resistance curves, on the other hand, is probably to be explained by the increasing number of atoms in the second condition.

(2) The temperature coefficient of liquid metals, which are to be thought of as largely in the second condition, would be expected to be less than that of a solid because the temperature coefficient of atoms in the second class is by themselves negative. In any actual liquid the negative temperature coefficient of the second-class atoms is modified by the atoms which are passing from the first to the second class, and which produce an effect of the opposite sign. If the total number of atoms in the second class is large enough to outweigh this other effect, the coefficient will be negative, as it is for liquid Cd and Zn. In any event, we expect the coefficient for the liquid to be less than for the solid, and in general to be less than $1/\tau$. The accompanying table shows this.

TABLE III.

Temperature Coefficient of Resistance of Liquid Metals.

Metal.	Temp. °C.	Temp. Coeff.	$\frac{1}{T}$.	Coefficient of Solid Extrapolated.
Na	100°	.00330	.00268	.00348
K	100	.00342	.00268	.00369
Al	657	.00051	.00107	
Cu	1100	.00037	.00073	
Sn	500	.00048	.00115	
Au	1100	.00045	.00073	
Hg	100	.00094	.00268	
Pb	500	.00044	.00115	
Bi	271	.00042	.00184	.0020±

Only two of the metals, K and Na which have low melting points, have

a coefficient greater than $1/\tau$, and for all the metals the coefficient of the liquid is less than that of the solid at the same temperature. The coefficients of the solids listed in the table were obtained by an extrapolation; the coefficients of the solids not listed are in all cases greater than $1/\tau$.

(3) If a liquid metal is heated at constant volume, the relative number of atoms in the two classes is probably little affected, and we would expect the temperature coefficient to be negative, if the number of atoms in the second group is larger than those of the first, as we suppose it is for a liquid. This is verified by the only liquid metal for which the data exist, liquid mercury. This observation was first made by Barus.[1]

(4) One meaning of a pressure coefficient of resistance for solids independent of temperature is that as temperature is increased at constant pressure (say atmospheric) the temperature coefficient at constant volume becomes more nearly negative, and if the same tendency persists will ultimately become negative, as it is for liquid mercury. This indicates that at higher temperatures the solid metal approaches a condition in which most of its atoms are in the second group, and is exactly what one would expect.

The fact that there is a tendency toward the behavior of the liquid may be seen on considering that the thermal expansion and the compressibility of a metal are both little affected by temperature at constant pressure, and that the relation between temperature and resistance is to a first approximation linear. This means that at high temperatures the same increment of pressure and temperature will be required to maintain volume constant as at low temperatures. The same increment of temperature will produce the same increment of actual resistance, but the decrement of resistance under a constant increment of pressure will increase, because the relative pressure coefficient is constant, while the actual resistance, on which the coefficient is calculated, becomes higher.

(5) The sudden drop of resistance of some metals at low temperatures has already been touched on. It means, according to this view, a clustering of the amplitudes closely about the mean.

(6) The negative pressure coefficient has already been explained at some length. It is primarily due to a decrease of atomic amplitude brought about by an increasing frequency at higher pressures. Added to this effect must be another effect, in most cases considerably smaller, due to the crowding of atoms from the second condition into the first. We have already seen that under ordinary conditions the number of atoms in the second condition is small, but in the case of liquid metals the number in the second condition is relatively larger, and we should

[1] C. Barus, Bull. U. S. Geol. Sur. No. 92, 1892, p. 74.

expect the decrease of resistance due to this cause to be higher. This is verified by the only liquid metal for which we have data, mercury.

(7) The decrease of relative pressure coefficient under increasing pressure is to be accounted for by the disappearance of atoms in the second class. This number is not large, and so the effect would be small, as it actually is. The rate of decrease of coefficient at rising pressures is a rough measure of the rate at which the atoms of the second group are being exhausted. If the rate of decrease of atoms of this group were constant at all pressures, we would, of course, have no decrease of the coefficient at higher pressures.

(8) The surprising fact that the decrease of coefficient with pressure is greater at low than at high temperatures is to be explained by the fact that at low temperatures the atoms of the second group are being exhausted more rapidly, since there are fewer of them, and therefore they contribute a more rapidly decreasing term to the negative pressure coefficient. The more rapid decrease at higher temperatures of some of the metals with low melting points is, on the other hand, probably to be explained by the greater decrease of the thermodynamic quantities which enter the formulas for the amplitude. It is for just these metals that one would expect the greatest decrease, although such a decrease has not yet been proved by experiment.

(9) When a metal is stretched by a mechanical tension the atoms are separated along the line of tension, but are brought closer together in a direction at right angles to the tension. We would expect therefore the number of gaps to increase if the path of the electrons is along the tension, but to decrease if it is at right angles. This corresponds with the observed changes of resistance under tension.

(10) The positive pressure coefficient of resistance of Bi and Sb next engages us. A positive pressure coefficient, according to this view, means that the number of gaps increases as volume decreases at constant temperature. Such an increase may be accounted for by an increase in amplitude, or what is the same thing, a decrease in frequency at constant temperature. A decrease in frequency with decreasing volume is not what we would expect, but may be brought into immediate connection with two other abnormal features of the behavior of Bi and Sb. Both Sb and Bi contract instead of expanding when melted, and the thermal expansion of both is unusually small. If a diagram is plotted of thermal expansion against compressibility (or melting point) of all the metals of these experiments, Sb and Bi will be found to occupy a position apart from the others, with abnormally small expansions. Now it is a conclusion most strongly suggested by the analysis of Debye, and also by my

own examination[1] of the properties of a gas composed of only one atom already mentioned, that the thermal expansion is intimately connected with the law of force between atoms. The subject has by no means been worked through as yet to a satisfactory conclusion, but we may probably assume with safety that an abnormally high thermal expansion means a restoring force increasing with unusual rapidity as the atoms are brought together, and that a small expansion means that the restoring force increases less rapidly than normal with decreasing volume. If we admit the conclusion as justified by the results above that the restoring force in normal metals is linear and independent of the volume, then for a substance with small expansion the restoring force decreases as the volume decreases. Such a decrease of restoring force means a decrease of mean frequency with decreasing volume, and hence an increase of amplitude. It is not difficult to imagine a law of force which will lead to such an unusual result.

In Fig. 1 is represented what we may suppose to be the action between three adjacent atoms. We suppose atom *B* to vibrate, and atoms *A* and *C* to remain at rest. The curve (1) shows the force with which *A* and *B* act on each other as a function of their distance apart. At infinite separation there is no force (indicated by the dotted horizontal line); as the atoms approach the force is at first an attraction, indicated by (1) lying above the horizontal line, but on closer approach the force rapidly becomes an intense repulsion. The law of force between *B* and *C* is precisely similar to that between *A* and *B* and is shown by the curve (2). The dotted part of curves (1) and (2) is what we may imagine for normal atoms, while the heavy curve is perhaps like that of Bi and Sb. The anomaly consists merely in a temporary acceleration of the rate of increase of the repulsive force followed by a retardation, as compared with the normal atom. The restoring force on *B* as it oscillates between *A* and *C* is evidently the difference of the forces exerted in opposite directions by *A* and *C*, and will therefore be proportional to the angle between (1) and (2) multiplied by the displacement of *B* from its equilibrium position. It is evident from inspection of the figure that as atoms *A* and *C* approach, that is as volume decreases, the angle of intersection between (1) and (2) decreases, and the restoring force therefore decreases. This decrease of restoring force means a small

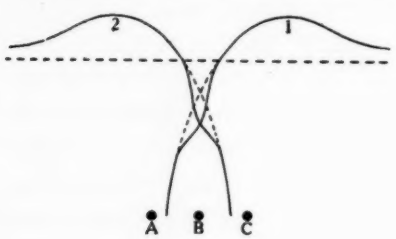

Fig. 1.

[1] P. W. Bridgman, Proc. Amer. Acad., 49, 107, 1913.

thermal expansion, and at the same time a decrease of frequency, and so an increase of resistance.

The slight anomaly in the law of force shown in Fig. 1 is also consistent with the solid having a larger volume than the liquid. To simplify the argument on this point suppose that the solid is at 0° Abs. We will try to show that the atoms are in equilibrium in a position of abnormally large volume. Equilibrium is found in that configuration in which the work done by the attractive forces during a virtual decrease of volume is exactly equal to the work done on the repulsive forces. We may suppose that the repulsive forces act only between immediately adjacent atoms, whereas all the more distant atoms exert attractive forces. Equilibrium will therefore be found where the few repulsive forces balance the many attractive forces. If there is a region in which the repulsive forces are unusually intense at an unusually large distance from the center of the atoms, as we have supposed the case for Bi and Sb, the repulsive forces will balance the attractive forces when the atoms are separated more than usual, and we will have a solid of abnormally large specific volume. If we suppose that this particular law of force is valid only when the atoms have the regular orientation of the crystal, but that the average law of force for haphazard orientations is more nearly normal, we have immediately a suggestion as to why the metal contracts on melting.

The abnormality we have imagined to account for the pressure effect has little effect on the temperature coefficient. The reason for this is that the temperature axis is very nearly normal to the line of constant amplitude in any event, so that a relatively large change in the direction of the line of constant frequency will produce a relatively small change in the temperature derivative of frequency. It is true that the temperature coefficients of resistance of Bi and Sb are not at all abnormal.

(11) The fact that the resistance of an alloy is always greater than that of its components is simply explained by the failure of the atoms of the two metals to fit closely together. In an alloy there are, therefore, a greater number of gaps permanently present than in the pure metal, and consequently the resistance is greater. As far as I know the conductivity of every alloy is less than that of its best conducting component, and in many cases is less than that of either component. The positive pressure coefficient of some alloys may be explained by supposing some such effect as that imagined for Bi, which is plausible enough if we are dealing with molecules instead of atoms, or by supposing that under the constraint of increasing pressure the atoms assume less natural positions, in which the number of gaps is greater. This latter alternative would be suggested by all my experiments on polymorphic transitions, in which the applica-

tion of pressure at constant temperature drives the molecules ultimately into such a configuration that some other configuration is more stable.

In conclusion a few critical remarks are not out of place. I do not offer the view of conductivity here explained as the only *possible* one consistent with all the facts, but merely as the one which seems to me at present most probable in the light of the facts now at our disposal. In one essential particular it does seem to me likely, however, that this view is like that which will be finally adopted. In the mechanism of conduction the properties of the atomic framework play a preponderating part; the atoms are not merely the trees of a forest among which a breeze of electrons plays, as in the classical free electron theory. The new experimental justification for this broad requirement in any new theory is the observation that the change of resistance is intimately connected with the amplitude of atomic vibration. Even if one is still so unconvinced of the truth of quantum theory as to be unwilling to admit the validity of the fundamental equations (1), (2) and especially (3), the fact cannot be escaped that we have found an approximate relation between the change of resistance and certain quantities of a purely thermodynamic character, which are certainly intimately connected with atomic properties.

This theory of conduction is not complete in the sense of the old free electron theory because it does not at present explain Ohm's law. We merely postulate, without searching for a detailed mechanism, that the electrons encounter resistance when they jump a gap between atoms, and that the resistance of the gap is on the average a resistance which obeys Ohm's law. This point is, however, probably one that it will not be difficult to meet. If, for instance, the force encountered by an electron in jumping a gap is like an ordinary fluid frictional force, proportional to the velocity, the requirements are met. The assumption of such a force is already familiar in various branches of electron theory.

The picture which I have presented of conduction in a metal is of a chain of electrons, which are normally at rest, getting under way under an applied electromotive force down a coherent chain of atoms, and gaining in speed until suddenly the continuity of the chain is interrupted by a break which appears somewhere between two neighboring atoms of the chain. The chain of electrons is not entirely stopped by the formation of the gap, but drives itself across by its own electromagnetic momentum, using up some or all of its store of energy in so doing. The gap absorbs the energy by a mechanism not specified, just as a spark absorbs the energy of an interrupted circuit, and from the gap the energy is ultimately absorbed as heat energy.

An alternative picture is that the gaps are not of sporadic, isolated occurrence as above, but that between every pair of neighboring atoms there is a resistance which on the average is proportional to the square of the mean amplitude. An objection to this view is that we must assume the square law, without at present even attempting to make it plausible, as we have above.

Still another point of view is possible, connecting so closely with the old free-electron theory as to account for Ohm's law. When the atoms are at rest at o° Abs. we may suppose that the electrons travel freely through the substance of the atoms, as the atoms of a gas freely traverse interatomic space, but as the amplitude of atomic vibration is increased, the electrons collide with the *gaps* between the atoms, precisely as they collided with the atoms on the old view. Ohm's law follows immediately, as on the old view. An objection to this viewpoint is that it brings up again the specific heat difficulty. We will have to suppose the electronic velocity independent of temperature, as does Wien. This does not seem to me a formidable difficulty; in fact such a constant velocity seems more plausible under the supposed circumstances than under the conditions imagined by Wien. For there must be some electrons always traversing the substance of the atoms as β-particles, continually emitted by the break-up of the outer ring of electrons in the atoms, and continually reabsorbed. Velocities from such a source as this must be independent of the temperature.

Wien's original picture of electrons passing freely through alley-ways between atoms is not a remote possibility consistent with a close connection between change of resistance and amplitude. The picture may contain much that is true, but probably the details of working out, as given by Wien, must be modified in any event. In particular Wien's assumption must be given up that at very low temperatures the quanta of energy are all located in a few isolated atoms, the rest of the atoms being at rest. It seems more probable now that the quanta are located in modes of elastic vibration. To explain the absence of any specific effect of a change of volume as such, we must suppose according to this view also that the atoms are distorted by pressure.

A combination of Wien's point of view with that advocated by this paper offers many attractive features: We may suppose that the electrons pass freely through the substance of the outer part of the atoms, encountering no resistance even when passing from atom to atom. The electron may, however, collide with the positive nucleus, which is so small that it acts like a point charge. The number of collisions will evidently be directly connected with the amplitude of oscillation of the nuclei.

According to this point of view the absence of any specific volume effect is not so serious a difficulty, because we would not expect it to be nearly as large. I do not at present, however, see the possibility of bringing into line with this view the wide range of facts dealt with qualitatively above.

The chief claim to consideration of the old free electron theory was that it offered an explanation for the Wiedemann-Franz ratio. Wien regretted as one of the weak points of his theory that he had to give up hope of explaining the Wiedemann-Franz ratio when he assumed electronic velocity independent of temperature. The view of conduction offered above does not attempt as yet to explain the Wiedemann-Franz ratio, but such an explanation does not seem to me beyond the bound of ultimate possibilities. In the first place, any mechanically consistent theory, irrespective of whether it assumes thermal conduction performed by electrons or not, must give a ratio involving the electronic charge in the correct way, simply by dimensional reasoning, but need not give the correct form for the coefficient of the charge. This is all the old theory does, the coefficient it predicts is not of the correct form. It is commonly held that because electrical conductors are so much better thermal conductors than electrical insulators the electron must play a large part in the thermal conduction of metals, and that therefore no theory can be correct which does not assign some part of the energy of temperature agitation to the electrons. This conclusion seems to me not necessary; all that is indicated is that the same mechanism which makes easy a transfer of electrons from atom to atom should also make possible an easy heat transfer. Now this is immediately indicated by the view above. Electrons pass freely from atom to atom without break of continuity when the outer parts of the fields of force of the atoms so merge that the effective individuality of the atom is lost. But when the atoms are so merged as to lose their individuality they will function as one large atom, and the energy of heat vibration will jump over whole ranks of atoms, as we know it must if the thermal conductivity of metals is to be accounted for by an atomic mechanism only.

SUMMARY.

The most important result of this paper is the observation that the variations of resistance of a normal solid metal are preeminently concerned with one factor only, the average amplitude of vibration of the atoms, irrespective of whether the change of amplitude is brought about by a change of pressure or of temperature. The proportional change of resistance is approximately twice the proportional change of amplitude.

This suggests that a successful theory of metallic conduction must discard the old viewpoint, which explained resistance in terms of the properties of an assemblage of electrons little affected by the inert framework of atoms, and substitute an explanation in terms of the properties of the atomic framework. There are several possible ways of giving such an explanation, of different physical complexions, all of them suggesting an intimate connection between resistance and amplitude. The view which I have adopted above seems to me that best adapted to bring into line the entire range of facts. This view is that the electrons normally pass freely from atom to atom, but if the atoms are separated beyond a critical distance, as by temperature agitation, gaps appear between the atoms which offer resistance. The resistance at ordinary temperatures is proportional to the number of gaps, and it is not unplausible to expect the change in the number of gaps to be twice the proportional change in the amplitude. At higher temperatures, however, that is large volumes, as in liquid metals, the passage of electrons from atom to atom is on the average difficult, but is facilitated by a collision of unusual violence. An increasing amplitude functions in opposite ways, therefore, at large and at small volumes. Under actual conditions there must be a combination of these two effects in varying proportions. I have shown in detail how the play against each other of these two different effects offers an explanation of the most important features of the behavior of both normal and abnormal metals.

Another point of extreme suggestiveness is that a pressure high enough to compress the metal to less than its volume at 0° Abs. is powerless to change its temperature coefficient of resistance. Consistency with the view advanced here seems to me to demand a distortion of the atom under pressure. Such a distortion has been suggested by many other aspects of my work on high pressures.

The experimental work on which this paper is based was assisted in large part by generous grants from the Bache Fund of the National Academy of Sciences and from the Rumford Fund of the American Academy of Arts and Sciences.

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[1] J. H. Jeans, Mathematical Theory of Electricity and Magnetism, Cambridge University Press, 1908, p. 133.

TOLMAN'S TRANSFORMATION EQUATIONS, THE PHOTO-ELECTRIC EFFECT AND RADIATION PRESSURE.

BY S. KARRER.

R. C. TOLMAN uses the following transformation equations when applying his principle of similitude,

$$l' = xl; \quad t' = xt; \quad e' = e; \quad m' = m/x; \quad S' = S.$$

P. W. Bridgman has pointed out that these equations are a particular case out of a large number of possible transformations which follow from the principle of dimensional homogeneity. Tolman has shown that, in many instances, the application of the above equations leads to results in accord with experiment. We wish to point out two important cases where the transformation equations give results which are in accord with present knowledge.

In the first place, let us assume we know from experiment that the kinetic energy E of the electrons emitted from a metal under the influence of light, minus a constant E_0 is only a function $f(n)$ of the frequency n of the incident light, and is independent of the intensity of the light and of the temperature and special properties of the metal. That is, assume

$$E - E_0 = f(n).$$

Then from the equations above it follows that

$$E' - E_0' = \frac{E - E_0}{x} \quad \text{and} \quad n' = \frac{n}{x},$$

$$E' - E_0' = f(n'),$$

$$\frac{E - E_0}{x} = f\left(\frac{n}{x}\right),$$

$$E - E_0 = xf\left(\frac{n}{x}\right) = f(n),$$

x being arbitrary, this functional equation must hold for every value of x. Its solution will be of the form,

$$f(n) = hn,$$

where h is a constant, hence

$$E - E_0 = hn,$$

which is Einstein's photoelectric equation. h must be determined by experiment; the measurements of Millikan give strong support to the correctness of this equation. And further, his results show that h is identical with Planck's radiation constant. From Tolman's point of view this is a very interesting result, but from the standpoint of Bridgman it is a necessary condition that the application of Tolman's equations give a correct result.

It is important to notice that Tolman's equations do not give any definite result in the case of the relation between the photoelectric current and the intensity of the light incident on the metal.

In the second place, we will apply the transformation equations to get the relation between the pressure exerted upon a body by the radiation incident upon it and the density of the radiation. Assume, experiment shows that the pressure p depends only on the energy density E of the radiation, then $p = f(E)$, and since

$$p' = \frac{p}{x^4} \quad \text{and} \quad E' = \frac{E}{x^4},$$

$f(E)$ must satisfy the following functional equation,

$$p = x^4 f\left(\frac{E}{x^4}\right) = f(E).$$

That is

$$p = f(E) = kE,$$

where k is a constant. As is well known, experiment shows that the radiation pressure is proportional to the energy density of the radiation.

SUMMARY.

Tolman's transformation equations lead to Einstein's law of the photoelectric effect if it is assumed that the kinetic energy of the electrons emitted from a metal, minus a certain constant, is only dependent upon the frequency of the incident light.

The equations also lead to the correct relation between the pressure of radiation and the density of the radiation.

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January, 1917.

ON THE PHOSPHORESCENCE OF THE URANYL SALTS.

BY EDWARD L. NICHOLS AND H. L. HOWES.

IN a recent paper[1] on the phosphorescence of the double salt uranyl ammonium sulphate, the following facts were established:

1. There is no appreciable change of color during decay.

2. The decay of phosphorescence is exceedingly rapid, the intensity falling to one thousandth of its initial value within .0035 second.

3. The very complex fluorescence spectrum at $-180°$ is identical in structure and relative distribution of intensities with that observed during the earlier and later stages of phosphorescence.

4. The curve of decay of phosphorescence differs from the prevailing type in that although as usual two successive processes are distinguishable, the second process is more rapid instead of being slower than the first.

The study of these phenomena has since been extended to several other typical uranyl salts, the curves of decay of which were determined by the method described in that paper and under conditions of excitation, etc., as nearly constant as possible. These curves of decay are of the same new type originally found in the uranyl ammonium sulphate. The two processes, as determined by the customary method of plotting $I^{-1/2}$ as a function of the time are indicated by straight lines differing from one another in slope and the second process has in all cases the steeper gradient. Later experiments in which the intensity of excitation was increased, revealed the presence of a third process not included within the interval of time covered by our earlier experiment.

STUDIES INVOLVING THE FIRST AND SECOND PROCESSES.

The curves shown in Figs. 1 and 2 are typical of the results obtained with all the salts under observation. They represent the decay of the phosphorescence of the following compounds:

Curve.	Substance.
1.	Uranyl ammonium sulphate
2.	Uranyl potassium sulphate
3.	Uranyl nitrate $+6H_2O$
4.	Uranyl sulphate
5.	Uranyl ammonium chloride

[1] Nichols, Proceedings of National Academy of Sciences, Vol. II., p. 328.

The initial intensity, under like excitation, varies greatly in the different salts as also, to some extent, does the rate of decay. It will be noted that the initial intensities of the ammonium and potassium sulphates

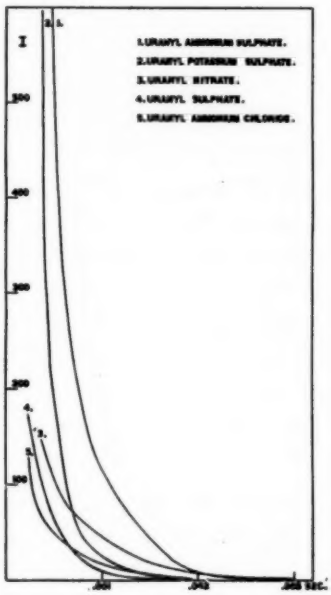

Fig. 1.

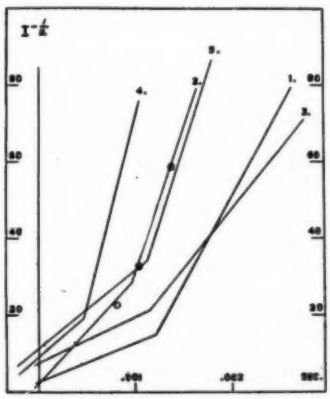

Fig. 2.

for example are several times greater than those of the nitrate, the sulphate and the ammonium chloride. This is however a question of previous history as well as of chemical and physical constitution as was determined in the following manner.

Uranyl potassium sulphate was dissolved in hot water and a mass of the minute crystals which were thrown down on cooling the solution were immediately sealed up in a glass tube. Care was taken throughout these manipulations to protect the precipitate from the action of light.

This sample, still in darkness, was mounted in the synchrono-phosphoroscope[1] and a curve of decay was taken, the first exposure to exciting light being that at the beginning of the run. The substance then showed temporarily, a brilliancy of phosphorescence much above that to be obtained under ordinary circumstances but was soon reduced to its normal and semi-permanent condition after which the usual curve of decay was obtained.

[1] For a description of this instrument, which was used in all the experiments recorded in this paper, except as otherwise stated, see the PHYSICAL REVIEW (2), VII., p. 586; also Science, V., XLIII., p. 937.

EXCITATION IN THE PRESENCE OF RED AND INFRA-RED RAYS.

To determine whether red or infra-red rays have an effect on these substances similar to that observed in the case of the phosphorescent sulphides a modification of the apparatus was made such that the surface under examination could be subjected to the intense illumination obtained by focusing the crater of an electric arc upon it. A screen of excellent ruby glass was interposed to cut off all but the longer waves and observations were made through a screen quite impervious to red.

Exposure to this source was found to affect measurably neither the brightness of fluorescence nor of phosphorescence nor the rate of decay. Curves taken after exposure to this source, those taken with the substance subjected to it interruptedly throughout the run, and curves in the determination of which readings were taken alternately with and without red light were all identical with those taken in entire absence from such exposures. The striking contrast between this negative result and the well-known effects of infra-red radiation upon the phosphorescence of the sulphides is notable.

The observations described in the note[1] already cited, showing the complete identity of the spectrum of fluorescence with that of phosphorescence seemed to indicate that the intensity would go over from that of fluorescence to that of phosphorescence without discontinuity. This conclusion was confirmed, within the errors of observation, by measurements just before and after the close of excitation. The only previous instances where this relation has been experimentally established so far as we know are to be found in Waggoner's[2] studies of phosphorescence of short duration and in our recent paper on the luminescence of kunzite.[3]

Where, as in these measurements, determinations have to be made through a very wide range and at exceedingly low intensities, doubts naturally arise as to the accuracy of the data for the lowest values. That in the present case the foot of the decay curves, where the brightness is reduced to a few thousandths of the initial intensity, is determined with a precision of the same order as that for higher values may be seen from Fig. 3 (Curve *BB*), in which the portion of the decay curve applying to the second process, *i. e.*, from .001 second onward, is plotted on a scale in which the ordinates for intensity are multiplied by ten. It will be noted that the observations fit the curve as closely as can be expected in work of this character. This is a fact quite in accord with previous

[1] Nichols, l. c.

[2] Waggoner, PHYSICAL REVIEW, XXVII., p. 209.

[3] Nichols and Howes, PHYSICAL REVIEW (2), IV., p. 26.

experiences in the domain of luminescence where observations made at the very lowest intensities which would permit of distinguishing the pattern in the contrast field of a photometer or spectrophotometer have been found quite as reliable as those in which the illumination was much more intense.

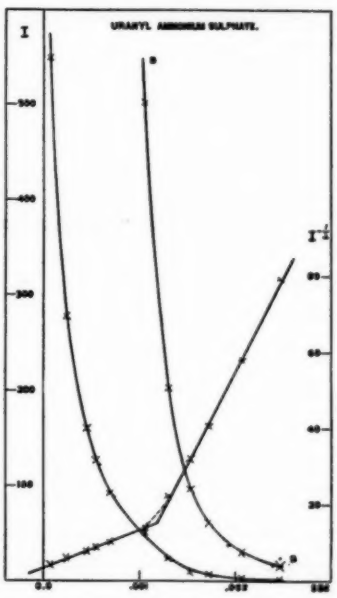

Fig. 3.

In view of the unexpected character of the decay curves for the phosphorescence of the uranyl compounds, the question arises whether the rather unusual mode of excitation employed; *i. e.*, periodically repeated exposures, 120 times a second to groups of sparks of high frequency, might produce such a result or whether the decay curves are characteristic of this class of compounds whatever the mode of excitation. It is true that both Waggoner[1] and Zeller[2] using a Merritt phosphoroscope found in their studies of phosphorescence of short duration that excitation by means of a spark discharge very similar to our own gave decay curves of the usual type.

It is also obvious from the measurements already described that the interval between excitation in our experiments, *i. e.*, 1/120 second is sufficient for the complete discharge of the phosphorescent glow and since the absence of any effect of red and infra-red indicates that there is no storage of undeveloped energy to be carried over, such as occurs in the phosphorescent sulphides, it seems probable that the decay curves do not vary greatly from that which might be obtained, were it possible to make the experiment, from a single exposure.

To test this a run was made upon the sample of uranyl ammonium sulphate previously used but with the Merritt phosphoroscope.

By driving the disk of this instrument 3,000 revolutions a minute, much the same range of time intervals was available as with the synchrono-phosphoroscope.

To further vary the conditions a quartz mercury arc was substituted for the spark gap of Waggoner and Zeller. The arrangement of apparatus was as shown in Fig. 4 in which *DD* is the revolving disk, *H* the mercury lamp, *P* the phosphorescent substance, *LB* the Lummer-Brodhun cube of

[1] Waggoner, PHYSICAL REVIEW, XXVII., p. 209.
[2] Zeller, PHYSICAL REVIEW, XXXI., p. 367.

the photometer, *SS* a color filter and milk glass screen. The device for shifting the oblique mirror *M* with reference to the aperture *A* in the disk is not shown.

Although the decay was somewhat more rapid in this determination on account of the less intense excitation; the curve was of precisely the type obtained by the previous method.

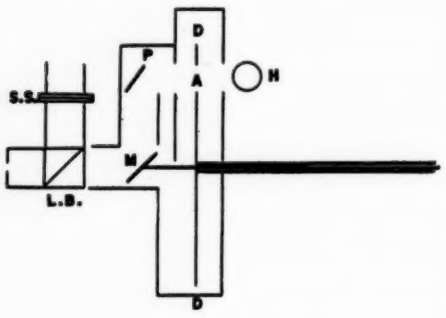

Fig. 4.

Measurements upon some of the bands of brief duration in the spectrum of the phosphorescent sulphides, recently made with the synchrono-phosphoroscope under experimental conditions identical with those described in this paper[1] yield curves of the usual type associated with these sulphides; so that the question of the change of form being due to the method employed is effectually eliminated. It is proposed, however, to further test the possible influence of the mode of excitation and method of measurement. For this experiment a phosphoroscope of the drum type, to be driven at very high speeds, is under construction.

SOLID SOLUTIONS AND SEMI-FLUIDS.

The uranyl salts differ from nearly all if not all phosphorescent substances hitherto studied. We do not have, as in the phosphorescent sulphides, the preparations of Waggoner, the ruby, etc., to deal with a trace of active material in solid solution but with compounds that are in themselves brilliantly phosphorescent. If the peculiar character of the curve of decay is due to that fact it might be expected that uranium glass, in which the active material is considered to be in a state of solid solution, would have a law of decay corresponding to the prevailing type for such solutions, *i. e.*, with the first process as indicated by the curve for $I^{-1/2}$ and time, represented by a line of steeper slope than the line for the second process. A piece of uranium glass gave, however, a decay curve similar to those of the uranyl salts (see Fig. 5). Another preparation which differs from most of the uranyl salts is the uranyl sodium phosphate, a sample of which was made by D. T. Wilber for certain studies in fluorescence recently published.[2] This substance is a very viscous liquid with the characteristic green fluorescence of the uranyl compounds.

[1] Nichols, Proc. Nat. Acad. Sciences, (1917).

[2] Howes and Wilber, PHYSICAL REVIEW (2), Vol. 7, p. 394, Mar., 1916.

Being a liquid one might expect, in accordance with the findings of Becquerel for liquids in general,[1] that there would be no observable after-glow. It is true that Bequerel expressed the belief that with a phosphoroscope of sufficient speed, phosphorescence would probably be detected in fluorescent liquids but no one, so far as we know, save Dewar in an unconfirmed statement concerning a supposed phosphorescence of liquid air, has since that time (1859) recorded an instance of phosphorescence excepting in solids and gases.

When a tube containing the phosphate was tested with the synchrono-phosphoroscope no phosphorescence was found of duration sufficient to be detected. Another sample so prepared as to reduce the amount of water to a minimum did however exhibit phosphorescence of measurable duration. This preparation, so slow was its rate of flow, might be regarded as a plastic solid rather than a viscous liquid. A bead of microcosmic salt, colored in the usual manner with uranium oxide, was comparable in its phosphorescence with canary glass.

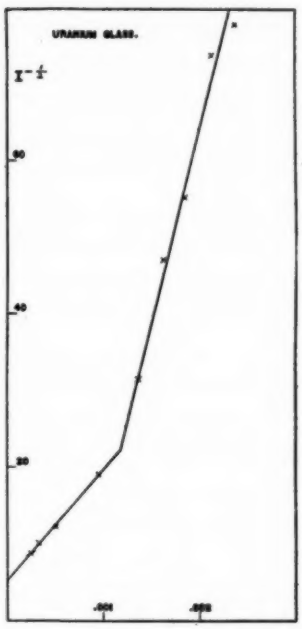

Fig. 5.

It appears that the persistence of luminescence is due to the consistency of the substance and disappears as the fluidity increases; also that the peculiar type of decay here described is common, not only to the crystalline uranyl salts in general but also to the gelatinous forms, as in this double salt and to substances in which uranium appears in solid solution as in the case of the canary glass.

The Third Process.

E. Becquerel[2] in the course of his great pioneer work on phosphorescence made a number of observations on the uranyl salts and on uranium glass. He noted the brilliant initial intensity and very rapid decay and to test the independence of the constant in his equation of decay when the illumination varied he made many measurements. If from his data we compute $I^{-1/2}$ as a function of the time we obtain curves of the same general form as those in Fig. 2.

Becquerel's observations are not numerous enough, taken by them-

[1] See E. Becquerel, La Lumiere, Vol. I., chapter on Phosphorescence.

[2] E. Becquerel, Annales de Chimie et de Physique (3), LXII., p. 1, 1861.

selves, to determine completely the type of curve. His measurements, however, cover a larger time interval than ours and the values for the longest times indicate an even more rapid decay following the second process. We had indeed found some indications of a similar tendency which had been omitted from our curves as lying almost beyond the range of definite determination.

To investigate the further trend of the curves of decay the intensity of excitation was increased by readjustment of the sparking circuit by which means it was found possible to extend the time interval for more than .006 sec. beyond the cessation of excitation.

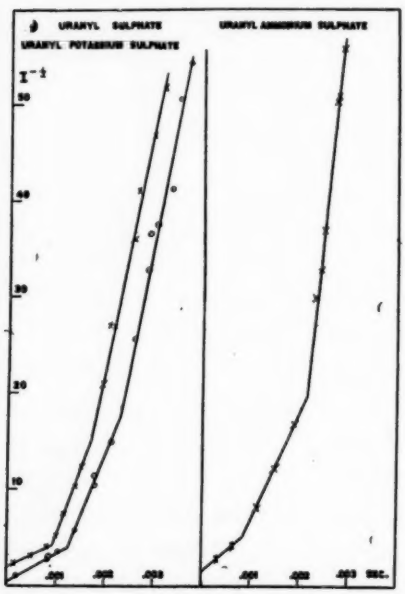

Fig. 6.

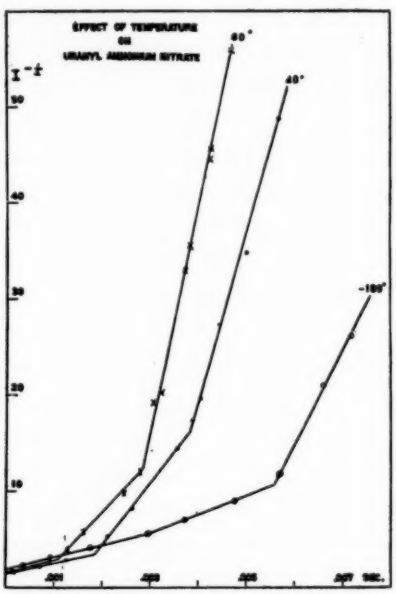

Fig. 7.

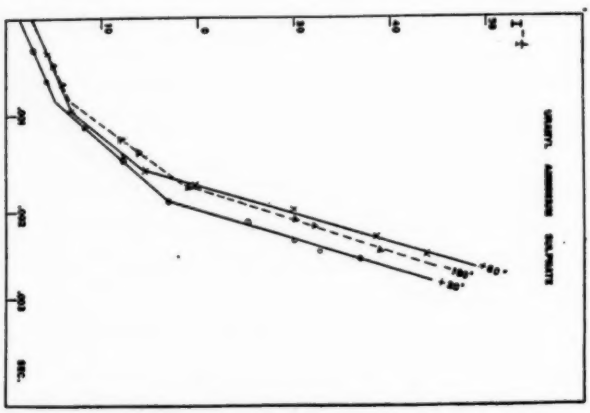

Fig. 8.

Careful, often repeated measurements, of the various salts showed in fact a third linear process beginning where our previous determinations had ceased and having a steeper slope, indicative of still more rapid decay. Typical results are indicated in Figs. 6, 7, 8, etc.

These processes may be numbered for convenience 1, 2 and 3 in the order in which they occur. Processes 1 and 2 are in general of about equal duration for a given salt. The abruptness of transition, however, varies greatly, and in some instances the change of slope is so gradual as to encroach seriously on process 2 at both ends.

THE INFLUENCE OF TEMPERATURE.

The only previous instances of decay of phosphorescence in which the later stages are more rapid than those preceding are noted by Ives and Luckiesh[1] in their study of the influence of temperature on phosphorescence, and by E. H. Kennard[2] in a more recent paper.

Ives and Luckiesh measured the phosphorescence of one of Lenard and Klatt's sulphides (BaBiK from Leppin and Masche). This substance was found to be very sensitive to change of temperature and the results at 0° C., 22° and 35°, when plotted for $I^{-1/2}$ any time in the usual manner, gave curves varying greatly in slope. The curve for O is concave towards the time axis, that for 22° linear and that for 35° *strongly convex*. They show that a linear relation may be obtained for each of these curves by varying the exponent of I.

The effect of temperature in the case of the phosphorescent sulphides, where one has to do with a composite of many overlapping bands of varying duration is undoubtedly different from that to be expected with the uranyl salts where the spectrum in spite of its complexity of structure is a unit. It was deemed of interest however to determine the effect of temperature upon the latter.

For this purpose a specimen of the uranyl ammonium nitrate was mounted within a cylindrical Dewar flask with unsilvered walls and its decay of phosphorescence was determined with the synchrono-phosphoroscope at a temperature a few degrees above that of liquid air (about −180°) at +20° and at +60°. The last-named temperature was maintained during the run by means of an electrical heating coil.

The principal change consists in a marked retardation of decay with lowering temperature (see Fig. 7), but this is not a universal characteristic of the uranyl compounds. Uranyl ammonium sulphate, for example (Fig. 8), is but slightly influenced in its rate of decay by change of tem-

[1] Ives and Luckiesh, Astrophysical Journal, XXXVI., p. 330 (1912).

[2] Kennard, PHYSICAL REVIEW (2), IV., p. 278 (1914).

perature and the curve for $-180°$ is intermediate between those for $+20°$ and $+60°$.

THE EFFECT OF VARYING THE INTENSITY OF EXCITATION.

To determine the effect of the intensity of excitation a series of measurements were made with the spark gap at various distances from the phosphorescent surface. The substance observed in these experiments was uranyl rubidium nitrate. It was found possible to make observations of the decay of phosphorescence with the excitation reduced to a two hundredth of that usually employed.

From the curves obtained of which four are given in Fig. 9, it will be

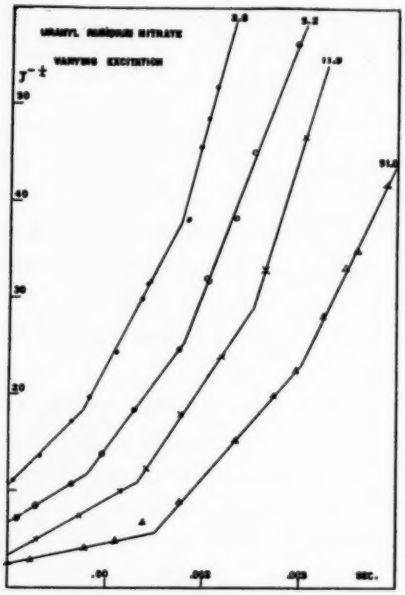

Fig. 9.

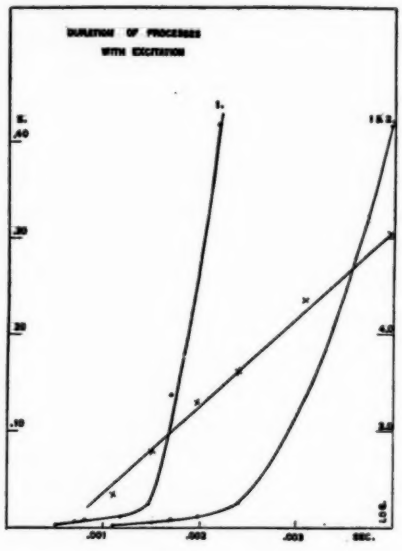

Fig. 10.

noted that all three processes are present whatever be the intensity of the exciting light; also that, taken roughly, processes 1 and 2 are of nearly equal duration and that with decreasing intensity of excitation the duration of each of these processes diminishes.

These relations are better shown in Fig. 10, in which the duration of process 1 and the sum of the durations of processes 1 and 2 counting from the close of excitation are plotted with the intensity of the exciting light as ordinates. Approximately in both cases the duration is proportional to the natural logarithm of the excitation. (See Table I.)

TABLE I.

Variation of Length of Processes with Excitation (Phosphorescence of Uranyl Rubidium Nitrate).

Intensity of Excitation (E).	Nat. Log E.	Duration.		
		Process 1.	Process 2.	Process 1 + 2.
41.70	6.033	.0022 sec.	.0018	.00400
13.70	4.919	.00170	.0014	.00310
2.52	3.220	.00147	.000993	.00240
1.35	2.590	.00118	.00080	.00198
0.900	2.190	.00080	.00090	.00170
0.476	1.560	.00070	.00076	.00146
0.201	0.698	.00050	.00060	.00110

This decrease in the duration of the two processes with falling excitation affords an obvious explanation of the varying character of the curves of decay of phosphorescent substances. Where the excitation is chiefly superficial, as in the case of some powders, the excitation may be nearly of one intensity and the curve made up of well-defined linear processes with sharp inflection points. We have found this to be the case in many instances. Where on the other hand fluorescence is excited within the crystalline mass by rays that have suffered considerable loss by absorption, etc., there will be a wide range of intensities of excitation and a curve results with distributed knees and linear processes shortened and sometimes almost obliterated. We observed this particularly where a clear crystal was mounted with faces perpendicular to the photometer and was excited from behind so that the light emitted by the surface nearest the exciting source passed through the crystal and was partially absorbed. Excitation occurred within the crystal in diminishing amount with increasing depth and the composite phosphorescence reaching the eue under such conditions showed this blending effect to a marked degree. The same crystal when excited from in front gave a curve in which the angles between processes were made more sharply defined. The effect in question is probably a general one and may well account for the perplexing differences in the curves of decay obtained under slightly varying circumstances. Thus one observer will obtain an angular curve where another, studying the same material, can detect no linear processes. The same observer, indeed, in attempting to repeat his measurements will often find the above-mentioned change of type under conditions which seem to be identical but in which the same relations as regards superficial and internal excitation are not preserved.

We found in the study of this effect a crystal one smooth face of which gave the blended curve while the opposite face, which was rough, gave

the angular curve, a change produced and reproducible by merely rotating the crystal through 180°.

THE PHOSPHORESCENCE OF VARIOUS NITRATES.

Observations were made on a series of nitrates previously prepared for the detailed comparison of the fluorescence spectra of that salt.[1] These consist of crystals with 6 H_2O (rhombic); 3 H_2O (triclinic) and 2 H_2O (system undetermined) as water of crystallization and a specimen sealed in glass which had been rendered as nearly anhydrous as was possible without decomposing the nitrate.

The curves of decay indicate a much slower rate of decay for the crystalline forms than for the anhydrous nitrate. Whatever effect the amount of water of crystallization may have is doubtless masked by the far greater influence of the crystalline form. This is perhaps to be expected since as has been shown in the paper just cited, these specimens exhibit as great differences in the structure and appearance of their fluorescence and absorption spectra as commonly exist between entirely distinct uranyl salts. That similar differences are found in the case of salts similar in composition but differing in crystalline form will be brought out in a forthcoming paper.

OBSERVATIONS ON POLARIZED PHOSPHORESCENCE.

Certain crystals of the double chlorides of uranyl exhibit fluorescence spectra consisting of sets of bands polarized at right angles to one another. To determine whether these components after the close of excitation decay independently or without change in their relative intensities, the following experiment was made.

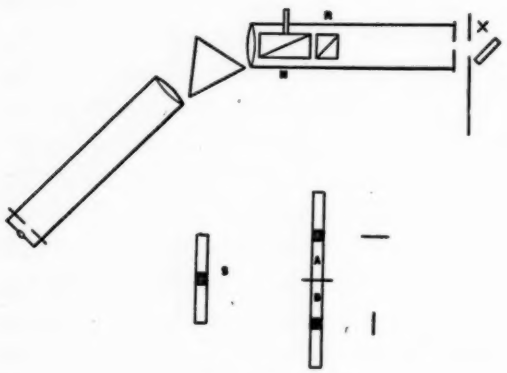

Fig. 11

A crystal of the rubidium uranyl chloride that exhibited the phenomenon of polarized fluorescence was mounted behind the disk of the synchrono-phosphoroscope and was observed with a spectroscope. The slit of the latter instrument was divided into two parts by means of an opaque strip across the middle (*S*, Fig. 11).

[1] Nichols and Merritt, PHYSICAL REVIEW (2), Vol. IX, p. 113 (1917).

Within the collimator a doubly refracting rhomb R and Nicol prism N were mounted. The rhomb gave two slit images vertically displaced and the adjustment was such that the lower part (A) of one image was contiguous with the upper part (B) of the other.

Thus two spectra of the phosphorescent field were obtained corresponding to the two polarized components. These presented the usual distinctive structures at whatever stage of the phosphorescent decay they were observed. By rotation of the Nicol prism the two fields could be brought to equal brightness for any given part of the spectrum and this balance, if made with the sector of the phosphoroscope set so as to give observations at .0005 second after extinction, was found equally correct up to .005 second or as long as phosphorescence was observable. The two components therefore decay at the same rate.

SUMMARY.

1. All uranyl salts thus far examined possess the same type of phosphorescence; *i. e.*, with increasing instead of diminishing rates of decay.

2. This is true not only of the crystalline forms but also of uranyl compounds in solid solution or in the plastic state characteristic of the double phosphates.

3. The initial brightness of phosphorescence under like excitation varies greatly with the different salts; as does also to some extent the rate of decay.

4. The brightness of a salt newly prepared in darkness is greater when first excited than subsequently but it soon reaches a nearly stable condition.

5. Exposure to red and infra-red rays is without effect as regards the rate of decay.

6. The phosphorescence, like the fluorescence of the uranyl salts appears to be independent of the mode of excitation and the structure of the intricate spectrum is the same during excitation and through the observable phosphorescent interval.

7. Changes in the rate of decay are not continuous but occur in definite steps there being at least three successive processes within the interval covered by observations, *i. e.*, about .006 seconds. These processes follow a law such that $I^{-1/2}$ is in linear relation to the time.

8. The first and second processes counting from the close of excitation are of nearly equal duration, increasing in duration with the intensity of excitation in such a manner that the duration of the process is approximately proportional to the natural logarithm of the excitation.

9. In certain salts, such as uranyl ammonium nitrate decay is retarded by cooling, in other cases the temperature effect is slight.

10. Uranyl nitrates with 2, 3 and 6 molecules of water of crystallization vary greatly in the rate of decay but the changes in crystalline form appear to be more important in this respect than the amount of water.

11. In the case of the polarized spectra of the double chlorides, both components decay at the same rate and no change in relative brightness could be detected throughout the range covered by observation.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
January, 1917.

NOTES ON THE CHANGE OF RESISTANCE OF CERTAIN SUBSTANCES IN LIGHT.[1]

By T. W. Case.

THE author has been making a systematic search for substances which show a change of resistance when exposed to light. The results of this search may prove interesting to those who are working in the same field, as several new light-active substances have been found.

Considerable work has already been done upon substances which change their resistance under the influence of light. The best known examples of this effect are selenium, stibnite and cuprous oxide, of which the latter has recently been announced by Professor A. H. Pfund, at Johns Hopkins, Physical Review, 7 (1916), 298.

As Professor Brown, of Iowa University, obtained much better results with a large crystal of selenium than had been obtained originally with the finely divided form, crystallized mineral specimens were used in this investigation where possible.

It may not be out of place here to give a description of the apparatus used, as it was simple and highly effective. It consisted essentially of an arc lamp and a variable speed water motor mounted upon a concrete base. The water motor drove a disk which had 15 sectorial openings; and so served to rapidly interrupt the beam of light produced by the arc, and brought to focus upon the substance under observation. Lead wires ran from this substance to an Ayrton shunt, which was connected to a three-step De Forrest Audion Amplifier. (The third step of this instrument was capable of increasing the energy of the original impulse 12,000 per cent.) High resistance receivers could be inserted in any one of these steps; and if any photoelectric action was produced by the interrupted beam of light, a distinct note would be heard in the receivers. The pitch of this note varied directly with the number of light interruptions per unit of time.

The crystal specimen under examination was held in a small clamp in the path of the interrupted beam of light. Contact was made at the ends of the crystal through the agency of thin platinum foil, which was pressed firmly against the crystal by a spring of variable tension in the

[1] The conditions of this experiment do not cover the minerals in all possible structures. Hence the negative actions are not necessarily conclusive.

Mineral.	Composition.[1]	Conductivity.	Action.
Sulphur.....		N.C.[2]	None
Selenium.....	Se	G.C.[3]	Fair, easily audible
Tellurium.....		G.C.	None
Antimony.....	Contains sometimes silver, iron or arsenic	G.C.	None
Bismuth.....		G.C.	None
Realgar.....	AsS	N.C.	None
Orpiment.....	As_2S_3	N.C.	None
Stibnite.....	Sb_2S_3	P.C.[4]	Small
Bismuthinite.....	Bi_2S_3	P.C.	Very good
Tetradymite.....	$Bi_2(TeS)_3$	N.C.	None
Molybdenite.....	MoS_2	G.C.	Fair
Domeykite.....	Cu_3As	G.C.	None
Algodonite.....	Cu_6As	G.C.	None
Whitneyite.....	Cu_9As	G.C.	None
Argentite.....	Ag_2S	G.C.	Good, large fatigue
Hessite.....	Ag_2Te	G.C.	None
Galenite.....	PbS	G.C.	Fair
Altaite.....	PbTe		None
Clausthalite.....	PbSe	G.C.	None
Berzelianite.....	Cu_2Se	N.C.	None
Crookesite.....	$(Cu, Tl, Ag)_2Se$	N.C.	None
Chalcocite.....	Cu_2S	N.C.	None
Stromeyerite.....	$(Ag, Cu)_2S$	N.C.	None
Sternbergite.....	Ag, Fe_2S_3	G.C.	None
Acanthite.....	Ag_2S	G.C.	Good, large fatigue
Sphalerite.....	ZnS	N.C.	None
Metacinnabarite..	HgS	G.C.	None
Guadalcazarite....	Found near above, contains a little zinc	N.C.	None
Cinnabar.....	HgS	N.C.	None
Covellite.....	CuS	P.C.	None
Greenockite.....	CdS	N.C.	None
Millerite.....	NiS	P.C.	None
Niccolite.....	NiAs	N.C.	None
Breithauptite.....	NiSb	P.C.	None
Pyrrhotite.....	$Fe_{11}S_{12}$	G.C.	None
Polydymite.....	Ni_4S_5	G.C.	None
Bornite.....	Cu_3FeS_3	G.C.	None
Linnaeite.....	Co_3S_4	G.C.	None
Chalcopyrite.....	$CuFeS_2$	G.C.	None
Stannite.....	$Cu_2.S.FeS.SnS_2$	G.C.	None

[1] The formulæ given for the minerals are those obtained from the mineral dealers; the order is that of Dana's System of Mineralogy.

[2] N.C. is used in this work as meaning that the substance is practically a non-conductor in the dark.

[3] G.C. indicates that a crystal of the substance one mm. on a side, in the holder used, at an applied potential of 110 volts has a resistance of less than 1 megohm.

[4] P.C. indicates that a crystal of the substance one mm. on a side, in the holder used, at an applied potential of 110 volts has a resistance greater than 1 megohm.

Mineral.	Composition.	Conductivity.	Action.
Hauerite.....	MnS_2	G.C.	None
Cobaltite.....	CoS_2CoAs_2	N.C.	None
Gersdorffite.....	NiAsS	G.C.	None
Corynite.....	Ni(AsSb)S	N.C.	None
Ullmannite.....	NiSbS	G.C.	None
Marcasite.....	FeS_2	G.C.	None
Arsenopyrite.....	FeAsS	G.C.	None
Pearceite.....	Ag_9AsS_6	G.C.	Fair
Sylvannite.....	(Au, Ag)Te_2	N.C.	None
Calaverite.....	(Au, Ag)Te_2	N.C.	None
Kermesite.....	Sb_2S_2O	N.C.	None
Zinkenite.....	$PbSb_2S_4$	G.C.	None
Sartorite.....	$PbAs_2S_4$	N.C.	None
Rathite.....	$3PbS_2As_2S_3$	P.C.	None
Emplectite.....	$CuBiS_2$		None
Chalcostibite.....	$CuSbS_2$	P.C.	None
Galenobismutite ..	$PbBi_2S_4$	G.C.	None
Miargyrite.....	$AgSbS_2$	G.C.	Fair
Plagionite.....	$5PbS.4Sb_2S_3$	N.C.	None
Schirmerite.....	$3(Ag_2Pb)S.2B_{12}S_3$	N.C.	None
Cosalite.....	$Pb_2B_{12}S_5$	G.C.	None
Jamesonite.....	$Pb_2Sb_2S_5$	P.C.	Fair
Kobellite.....	$Pb_2(BiSb)_2S_5$	P.C.	None
Semseyite.....	$Pb_7Sb_6S_{16}$		None
Freieslebenite.....	$(Pb, Ag_2)_5Sb_4S_{11}$	P.C.	None
Bournonite.....	$3(Cu_2, Pb)S.Sb_2S_3$	P.C.	Good
Boulangerite.....	$Pb_3Sb_2S_6$	N.C.	Good
Fizelyite.....	$Ag_2Pb_5Sb_8S_{18}$	N.C.	None
Guitermanite.....	$10PbS.3As_2S_3$	N.C.	None
Pyrargyrite.....	Ag_3SbS_3	P.C.	Fair
Proustite.....	Ag_3AsS_3	G.C.	Good
Tetrahedrite.....	$Cu_8Sb_2S_7$	G.C.	None
Stephannite.....	Ag_5SbS_4	G.C.	Fair
Polybasite.....	Ag_9SbS_6	G.C.	Fair
Enargite.....	$3Cu_2S.As_2S_5$	N.C.	None
Epiboulangerite...	$Pb_3Sb_2S_6$	N.C.	None
Cerargyrite.....	Silver Chloride	N.C.	None
Iodyrite.....	AgI	P.C.	Fair
Fluorite.....	CaF_2	N.C.	None
Laurionite.....	$PbCl_2.Pb(OH)_2$	N.C.	None
Cumengeite.....	$PbCuCl_2(OH)_2$	N.C.	None
Quartz (tiger eye) .	SiO_2	N.C.	None
Valentinite.....	Sb_2O_3	N.C.	None
Bismite.....	Bi_2O_3	N.C.	None
Molybdite.....	MoO_3	N.C.	None
Cervantite.....	Sb_2O_4	N.C.	None
Cuprite[1].....	Cu_2O	P.C.	Fair
Chalcotrichite.....	Cu_2O	N.C.	None

[1] Cuprite was predicted to show this action by Professor A. H. Pfund (PHYS. REV., 7 (1916), 298).

Mineral.	Composition.	Conductivity.	Action.
Silver oxide	Ag_2O (pastiles freshly prepared)	P.C.	Fair
Periclasite	MgO	N.C.	None
Manganosite	MnO	P.C.	None
Zincite	ZnO	N.C.	None
Massicot	PbO	N.C.	None
Tenorite	CuO	P.C.	None
Corundum	Al_2O_3	N.C.	None
Hematite	Fe_2O_3	G.C.	None
Ruby spinel	$MgAl_2O_4$	N.C.	None
Magnetite	$FeO.Fe_2O_3$	G.C.	None
Franklinite	$(FeZnMn)O(FeMn)_2O_3$	P.C.	None
Chromite	$FeCr_2O_4$	P.C.	None
Chrysoberyl	$BeAl_2O_4$	N.C.	None
Hausmannite	Mn_3O_4	N.C.	None
Minium	Pb_3O_4	N.C.	None
Cassiterite	SnO_2	G.C.	None
Rutile	TiO_2	N.C.	None
Brookite	TiO_2	N.C.	None
Pyrolusite	MnO_2	G.C.	None
Turgite	$Fe_4H_2O_7$	G.C.	None
Diaspore	$Al_2O_3.H_2O$	N.C.	None
Göthite	FeO(OH)	N.C.	None
Limonite	$2Fe_2O_3.3H_2O$	N.C.	None
Brucite	$MgO.H_2O$	N.C.	None
Gibbsite	$Al(OH)_3$	N.C.	None
Chalcophanite	$(Mn, Zn)O.2MnO_2.2H_2O$	N.C.	None
Psilomelane	H_4MnO_5	N.C.	None
Lampadite	MnO_2	P.C.	None
Calcite	$CaCO_3$	N.C.	None
Siderite	$FeCO_3$	N.C.	None
Smithsonite	$ZnCO_3$	N.C.	None
Phosgenite	$PbCO_3.PbCl_2$	N.C.	None
Malachite	$CuCO_3\ Cu(OH)_2$	N.C.	None
Azurite	$2CuCO_3\ Cu(OH)_2$	N.C.	None
Aurichalcite	$2(Zn, Cu)Co_3.3(Zn, (Cu)(OH)_2$	N.C.	None
Microcline	$KAlSi_3O_8$	N.C.	None
Albite (soda feldspar	$NaAlSi_3O_8$	N.C.	None
Actinolite	$(CaMgFe)SiO_3$	N.C.	None
Beryl	$Be_3Al_2Si_6O_{18}$	N.C.	None
Garnet	$Ca_3Al_2Si_3O_{12}$	N.C.	None
Dioptase	H_2CuSiO_4	N.C.	None
Zircon	$ZrSiO_4$	N.C.	None
Cyrtolite	(Altered zircon)	N.C.	None
Gadolinite	$Be_2FeY_2Si_2O_{10}$	N.C.	None
Zoisite	$Ca_2(AlOH)Al_2(SiO_4)_3$	N.C.	None
Epidote	$HCa_2(Al, Fe)_3Si_3O_{13}$	N.C.	None
Prehnite	$H_2Ca_2Al_2Si_3O_{12}$	N.C.	None
Chrondrodite	$H_2Mg_{10}Si_5O_{24}F_4$	N.C.	None
Tourmaline	R_6SiO_5	N.C.	None

Mineral.	Composition.	Conductivity.	Action.
Staurolite.....	$H_4(FeMg)_6(AlFe)_{24}Si_{11}O_{66}$	N.C.	None
Apophyllite.....	$H_7KCa_4(SiO_3)_8$ and $4\frac{1}{2}H_2O$	N.C.	None
Stilbite.....	$H_4(Na_2.Ca)Al_2Si_6O_{18}$ and $4H_2O$	N.C.	None
Laumontite.....	$H_4CaAl_2Si_4O_{14}$ and $2H_2O$	N.C.	None
Penninite.....	$Hg(Mg, Fe)_5Al_2Si_3O_{18}$	N.C.	None
Talc.....	$H_2Mg_3Si_4O_{12}$	N.C.	None
Sepiolite.....	$H_4Mg_2Si_3O_{10}$	N.C.	None
Pyrophyllite.....	$Al_2Si_3O_9$ and H_2O	N.C.	None
Thaumasite.....	$CaSiO_3.CaCO_3.CaSO_4.15\ H_2O$	N.C.	None
Perovskite.....	$CaTiO_3$	N.C.	None
Columbite.....	$FeCb_2(Ta)_2O_6$	N.C.	None
Samarskite.....	$R_3R_2(Nb, Ta)_6O_2$	P.C.	None
Euxenite (columbate yttria).....	$R(NbO_3)_3\ R_2(TiO_3)_3$ and $3/2\ H_2O$	N.C.	None
Vanadinite.....	Pb_3V 1/3 PbCl	N.C.	None
Olivenite.....	$Cu_3As_2O_8$:$Cu(OH)_2$	N.C.	None
Descloizite.....	$Pb_2O_2VO_3$	N.C.	None
Vivianite.....	$Fe_3P_2O_8$ and $8H_2O$	N.C.	None
Torbernite.....	$Cu(UO)_2P_2O_8$ and $8H_2O$	N.C.	None
Barite.....	$BaSO_4$	N.C.	None
Crocoite.....	$PbCrO_4$	P.C.	None
Wulfenite.....	$PbMoO_4$	N.C.	None
Aguilarite.....	$AgSAg_2Se$	N.C.	None
Chalcedony.....	SiO_2	N.C.	None
Copalite.....	(Fossil Copal)	P.C.	None
Lorandite.....	$TlAsS_2$	N.C.	None
Smoky quartz.....	SiO_2	N.C.	None

clamp. An E.M.F. of 110 volts was placed in series circuit with the crystal, the audion apparatus and a protective resistance. In the work with very fragile crystals the clamp was replaced by a mounting of the crystal upon a small cork, current being sent through the specimen through the agency of gold leaf contacts at the ends of the crystal.

In some instances, the resistance of the crystal under examination was such that the impressed voltage allowed either too much or too little current to flow through the apparatus. With low resistance crystals this was taken care of by the shunt. With crystals of very high resistance the voltage and size of the crystal were adjusted until the desired current was obtained. A list of the minerals examined, an indication of their photo activity as determined by the note on the receivers, and their relative conductivity in the dark as shown on pages 305–309.

The active substances are being further studied in regard to their resistance changes, fatigue, deduction and induction periods. Two specimens which show remarkable action are acicular crystals of bismuth sulphide (bismuthinite), and a granular lead antimony sulphide. It

suffices to say here that the resistance of a piece of the latter 1 mm. by 10 mm., reduces about 5,000 per cent. from the value in the dark in dull sunlight at an applied potential of 110 volts. If the substance be actually heated up, either by exposure to heat or passing a current which slowly heats the substance, then the resistance is gradually lowered, but this is a slow process. All of the photo active sulphides show the quick light reaction in the red part of the spectrum. Both the bismuthinite and the lead antimony sulphide give fine results when used as a transmitter in a photo phone system, using a manometric flame for transforming the voice variations into light variations. The voice reproduction is very clear and loud. Specimens of lead antimony sulphide at present show no evidence of an induction period or fatigue, outside of the slow heating effect due to the current which reaches an equilibrium after several hours, after which the light reaction then becomes constant. This, as well as its large change of resistance with small variations of light intensity allow it to be used as a very deliçate actinometer.

SUMMARY.

1. An apparatus has been described for the detection of certain photo electric phenomena.

2. The change of resistance of certain substances in light are being studied; and a number of new compounds have been found which show a change of conductivity in light.

AUBURN, N. Y.

AN IMPROVED HIGH VACUUM MERCURY VAPOR PUMP.

BY CHAS. T. KNIPP.

THE diffusion pump of Gaede[1] has stimulated a number of investigators in this country to enter the field of pump design with the result that several improvements involving new principles have been published. In a recent number of the PHYSICAL REVIEW Langmuir[2] describes an improved mercury vapor pump "characterized by its extreme speed and the high degree of vacuum attainable." The writer of this note being interested for a number of years in the production of high vacua also seized upon this opportunity to aid, if possible, in simplifying the means by which vacua are produced in the research laboratory and submits the following design made wholly of glass as an improved high-vacuum high-speed mercury vapor pump.

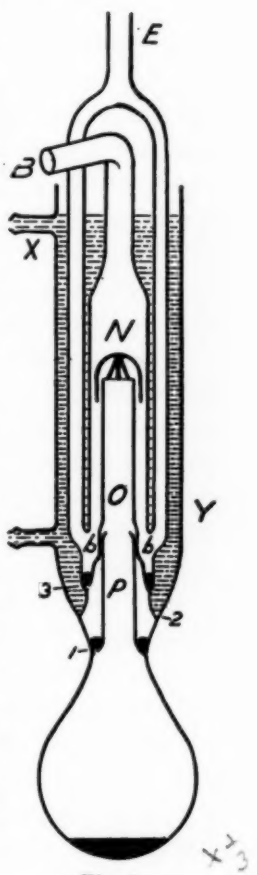

Fig. 1.
An improved high vacuum mercury vapor pump.

The pump complete, except the usual mercury vapor trap, is shown in the figure, which is one third full size. The bulb to be exhausted and trap are fused to B, while the tube E is attached to the supporting or rough pump. The mercury vapor rising from the lower bulb, which is heated in a sand or heavy oil bath, streams up through the short tubes P and O and is deflected downward through an annular throat by the umbrella N. The issuing mercury vapor at once condenses on the water-cooled surface of the enveloping tube and, as Langmuir[3] pointed out, the gas that comes from B is forced mechanically downward from the lower edge of N along the cooled surface of the condensing chamber. This accumulated gas is removed through the lateral tubes $b\ b$, which unite at the top and form the exhaust tube E, all being enveloped by the water jacket XY, as shown in the figure. This construction keeps the

[1] Ann. Physik, 46, 357, 1915.
[2] PHYS. REV., 8, 48, July, 1916.
[3] Gen. Elect. Rev., 19, 1060, Dec., 1916.

mercury, which collects at the ring-seal 3, cool, and thus removes the objection that mercury vapor having an *upward* velocity would enter the annular condensing chamber. A small opening shown at 3 serves as a valve which allows the accumulated mercury to pass, yet due to surface tension maintains a perfect seal. The short tube *P* is inserted to shield the hot mercury vapor streaming up from the boiler from condensing on the surfaces at 3. The upper end of *P* telescopes loosely into the lower end of *O*, while the lower end is secured by the ring-seal 1, having also a small valve opening in it through which the mercury passes back into the boiler. By making the upper end of *P* conical condensed mercury vapor is caught in the annular space thus formed and automatically seals the space *PO* from the cavity just outside of *P*. The cold mercury collected at the ring-seal 3, and the adjacent water-jacket, thus have but little opportunity of cooling the hot stream of mercury vapor passing up through *PO*, and, furthermore, the temperature gradient between the ring-seals 1 and 2, and 3 and *b b* are not abrupt, hence there is no danger of the glass cracking. This construction very much simplifies the glass-blowing, since the tube throughout the process is kept perfectly symmetrical.

In the absence of a convenient means of measuring the pressure within the discharge vessel quickly, the writer has chosen to express the degree of exhaustion in terms of the cathode dark space and the sparking distance at a parallel gap in air. The induction coil used was a 10 cm. spark Kohl coil, and the parallel gap was between balls 1.75 cm. in diameter. The supporting pump was a Gaede rotary mercury pump backed by a Gaede oil box pump. The mercury was heated in an oil bath by one bunsen burner. The trap beyond *B* was immersed in liquid air. Mercury vapor pumps are not sensibly operative until the vacuum drawn by the supporting pump is of the order of 1 cm. Crookes dark space, depending upon the construction of the pump as regards annular throat, etc. Hence the test for speed should not be from atmospheric pressure. The following tests serve to give an indication of the speed attainable.

Test 1.—With the discharge vessel fused to *B* (through a centimeter tube 30 cm. long) having a volume of 270 c.c. it required, by repeated trial, 29 minutes to lengthen the dark space from 1 cm. to 5 cm. equivalent spark in air; while with *the mercury vapor pump operative it required but 43 seconds.*

Test 2.—With a 6 liter vessel attached by a short large-diameter tube, it required 51 minutes to range from 1 cm. dark space to an equivalent parallel gap in air of 4.65 cm.; which time interval with *this pump*

operative was reduced to 2½ minutes. At the end of another 2 minutes the vacuum was so hard that the 10 cm. Kohl coil was not able to force a discharge.

The advantages of this form of hot blast mercury vapor condensation glass pump may be briefly stated as

1. The symmetrical design simplifies the glass-blowing.
2. Full effectiveness of the hot blast of mercury vapor without sensible loss of heat through a long delivery tube.
3. Effective cooling by a proper placing of water-jacket, ring-seals, and of an internal shielding tube.
4. The use of simple mercury valves for the direct return of the condensed mercury vapor to the boiler.

Laboratory of Physics,
University of Illinois,
January 15, 1917.

ELECTRODE POLARIZATION IN GASES.

BY C. A. SKINNER.

IN a recent article[1] I have described experiments which show beyond doubt that there exists a large polarization P. D. between the cathode and the conducting gas of a glow current; and which, at the same time, prove the reliability of wire sound measurements of potential in the "Crooke's dark space," where the error, if any, should be the greatest.

These experiments force the conclusion that, as indicated, by wire sound measurements, there exists in general a polarization P. D., at the anode as well as at the cathode, wherever the current is transmitted from the gas to the electrode by ionic carriers. If the anode be placed in the negative glow its polarization P. D. practically vanishes[2] presumably because there the current is transmitted to it by free electrons, which probably do not produce much of a polarization. Outside the negative glow the anode polarization is about 20 volts. These facts together with Chrisler's experiments on anode absorption[3]—which show that in general the negative carriers in the glow current are atoms—leads to the interesting conclusion that the electrons must become largely attached to the atoms shortly after leaving the negative glow.

Lacking any free positive electrons, there is naturally no part of the ordinary glow current where the cathode polarization vanishes. It is found to be of the same magnitude in the negative glow as at the main cathode. Only when the current is made up entirely of free electrons —and possibly ions freed from the electrodes instead of discharging to them—can one assume that no polarization exists at the electrodes. Such a condition obtains approximately at the cathode in the ordinary arc, at both electrodes in the mercury arc, and at a Wehnelt cathode.

Important errors have undoubtedly been made in various experimental determinations where the existence of a polarization, especially at the cathode, has been ignored. An interesting optical corroboration of this fact has been recently observed by Tate, in which he vainly attempted to shorten the single line radiation from mercury by applying, as he supposed, a back field parallel to his spectroscope slit to slow down the

[1] C. A. Skinner, PHYS. REV., February, 1917.
[2] C. A. Skinner, Phil. Mag., 6, 2, p. 616, 1901.
[3] V. L. Chrisler, Physik. Zeitschr., 10, p. 745, 1909.

electrons. He finally found that his supposed back field did not exist, except as a polarization potential difference at the cathode. All those experiments are subject to such an error, where a theoretical potential has been supposedly impressed on a conducting gas by two metal electrodes charged to a definite potential difference.

In the previous article (l.c.) the following law was found with an aluminum cathode placed in the negative glow of a separate ionizing current through hydrogen:

$$V_b = g\left(\frac{j}{n}\right)^2, \qquad (1)$$

where V_b is the polarization P. D. and j the current density at the cathode, n the number of positive ions per c.c. in the gas surrounding the cathode and g a constant. This law fits satisfactorily for values of V_b above about 10 volts,[1] and also holds at the main cathode.

In this article is given a simple mathematical theory, with experimental applications, of this electrode polarization as arising from an elastic rebound of the discharging ions from the electrode. An earlier attempt was made to solve the same problem from the same viewpoint. The greater simplicity and applicability of the present theory, as compared with the former, is largely due to the fact that we have not sought to express here the distribution of potential, but have related other magnitudes.

In the earlier theory the polarization region was *assumed* to extend one mean free path of the discharging ion from the electrode. Our empirical equation (1) is however independent of the gas pressure. This fact, together with other general considerations, has led to the conviction that the extent of the polarization region from the electrode is but a small part of a mean free path of the discharging ions. This view simplifies any theoretical treatment of the subject to the extent that the chance of collision between the discharging ions and the gas molecules need not be considered.

Theory.

The simple law expressed by equation (1) will first be derived. This has been found to hold with aluminum in hydrogen for values of V_b above 10 volts. It will then be shown that the deviation from the law observed below 10 volts may be satisfactorily ascribed to the temperature velocity of the discharging ions.

Case in which the Temperature Velocity of the Discharging Ions is

[1] The apparent deviation for values of V_b above about 80 volts is probably due to the increase in n arising from the ionization produced by electrons freed from the transverse cathode.

Negligible.—On the average the discharging ions enter the polarization region with the kinetic energy which the electric field imparts to them on their last mean free path λ outside that region. Let the drop of potential over this last mean free path be E_λ and the polarization P. D. be V_b. The ion strikes the electrode with the kinetic energy equal to

$$(E_\lambda + V_b)e,$$

where e is the ionic charge. By impact on the electrode it loses on the average a fraction k' of this energy, rebounding with a kinetic energy equal to

$$(1 - k')(E_\lambda + V_b)e.$$

The polarization P. D. arises from the consequent accumulation of the discharging ions, hence its outer boundary is reached by those ions on their first rebound which are reflected in a direction normal to the equipotential surfaces. Their turning point is where all their kinetic energy of rebound is converted into the potential energy $V_b e$. We have then

$$V_b e = (1 - k')(E_\lambda + V_b)e; \tag{2}$$

hence

$$V_b = \frac{1 - k'}{k'} E_\lambda. \tag{3}$$

But we have similarly the relation

$$E_\lambda e = \tfrac{1}{2} m\overline{u^2}, \tag{4}$$

where $\frac{1}{2}m\overline{u^2}$ is the mean kinetic energy of the ions on their entrance to the polarization region. Substituting from (4) in (3)

$$V_b = \frac{1}{2}\frac{m}{e} \cdot \frac{1 - k'}{k'} \cdot \overline{u^2}. \tag{5}$$

To compare this expression with the empirical equation (1) we introduce the condition that the electric current to the polarization region is carried entirely by the discharging ions. This holds very accurately under ordinary glow current conditions. Then

$$j = neu, \tag{6}$$

in which j is the current density, n the number of discharging ions per c.c. just outside the polarization region, and u their average velocity at that point. Obviously u is proportional to $\sqrt{\overline{u^2}}$, so that, from (5) and (6)

$$V_b = \frac{1}{2} \cdot \frac{m}{e^2} \cdot \frac{1 - k'}{k^1} \cdot g' \cdot \left(\frac{j}{n}\right)^2, \tag{7}$$

where

$$g' = \frac{\overline{u^2}}{u^2}.$$

Equation (7) is identical in form with the empirical equation (1).

Inasmuch as it has been shown in the previous article that (1) fits not only the conditions at the transverse cathode, but also expresses the previously discovered law for the main cathode, we will turn our attention here to the determination of k'. From (2)

$$k' = \frac{E_\lambda}{E_\lambda + V_b}. \tag{8}$$

From this equation the values of k' have been calculated for cathodes of several metals in hydrogen, nitrogen, and oxygen—the values of E_λ and V_b having been obtained from measurements made by Cheny[2] Neuswanger[2] and myself[3]—the value of λ being taken as the m.f.p. of the molecule. These are incorporated in Table I. The values of k'

TABLE I.

Values of k'.

Cathode.	Current Density.	Hydrogen.			Nitrogen.			Oxygen.		
		V_b.	E_λ.	k'.	V_b.	E_λ.	k'.	V_b.	E_λ.	k'.
Aluminum.....	"Normal"	78	2.3	.030	94	3.2	.033	167	4.7	.027
	2×"Normal"	101	2.6	.025	112	3.8	.033	207	5.1	.024
	4×"Normal"	130	3.6	.027	128	4.4	.033	248	6.1	.024
Platinum.....	"Normal"	143	2.2	.015						
Nickel.....	"Normal"	174	2.4	.0135						
Steel.....	"Normal"	155	2.2	.014						

are found to vary but little with considerable variation in current density, polarization P. D. and gas pressure—though the effect of the latter is not brought out in the table. In hydrogen k' is about twice as large with aluminum as with platinum, nickel or steel—for which metals it is nearly the same. For aluminum in the different gases an appreciable difference in k' is found, but it is not large.

It should be remarked that k' is derived from average conditions, while the border of the polarization region is really marked by those ions which rebound farther than the average. In that case k' should not necessarily give the actual fractional loss of energy on impact, but merely be proportional to it. The factor of proportionality should be the same however for the different gases and metals, since the relation is in terms of the m.f.p. of the ions.

Under the discussion of the temperature effect a method is given for determining the real value of loss by impact on the electrode.

[1] W. L. Cheny, PHYS. REV., VII., p. 241, 1916.

[2] Wm. Neuswanger, PHYS. REV., VII., p. 253, 1916.

[3] C. A. Skinner, PHYS. REV., VI, p. 158, 1915.

Effect of a Temperature Velocity of the Discharging Ions.—A distinct deviation from the simple theoretical equation (7) or (1) is found when polarization potentials below 10 volts are used. This is best seen in the curve of apparent cathode resistance R_b as in Fig. 1.

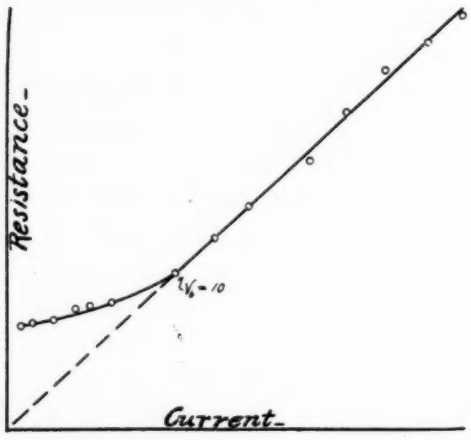

Fig. 1.

From (1)

$$R_b = \frac{V_b}{j}$$

$$= \frac{gj}{n^2}.$$

For constant n the apparent resistance should be a straight line from the origin. For values of V_b below 10 volts the resistance is observed to deviate rapidly toward a constant magnitude as the current is reduced. That is to say, for low values of V_b the number of ions discharging to the cathode, in a given time, is less than the derived law requires.

We assume that with polarizing potentials below 10 volts the law of distribution of potential between the transverse electrodes is the same as above 10 vlots. Then the number of discharging ions which *enter* the polarization region in a given time will be that determined by the simple law. If now, the current be smaller than the law requires, it is because a part of the ions rebound from the electrode with a sufficient component velocity to carry them out of the polarization region again. The origin of this excess velocity is conceived to be in the temperature of the ions.

Let n'/n be the fractional part of the ions entering the polarization region, which escape from it again. Then equation 6 becomes

$$j = (n - n')eu \qquad (9)$$

and consequently (7) becomes

$$V_b = \frac{1}{2} \cdot \frac{m}{e^3} \cdot \frac{1 - k'}{k'} \cdot g' \left(\frac{n - n'}{j} \right)^2$$

or in terms of (1)

$$V_b = g \left(\frac{j}{n - n'} \right)^2. \tag{10}$$

From this

$$\frac{n'}{n} = 1 - \left(\frac{g}{V_b} \right)^{\frac{1}{2}} \frac{j}{n}. \tag{11}$$

This quantity n'/n represents the fractional part of the entrant ions which, after impact on the electrode, have a sufficient component velocity normal to it to carry them out of the polarization region again. From the law of velocity distribution and the value of n'/n we can calculate the lowest component temperature velocity with which this fraction of the ions enter the polarization region. Those having the lowest velocity possess sufficient component velocity outward, after impact, to just take them out of the polarization region again. Having the entrant velocity and the emergent velocity we can determine the loss on impact.

It is first necessary however to assume the kind of reflection—whether it be diffuse, regular, or of special form. To avoid lengthening the discussion it may be simply stated that, on the basis of a single impact and no collision between the ions within the polarization region, the magnitudes involved render diffuse reflection impossible. As a special form of reflection we will consider, along with regular reflection, the case in which the polarization region fits the surface of the electrode like a skin, approximating a spherical form about each point of impact. Then any direction of rebound tends to carry the ion out of the polarization region. In that case only the actual speed of the molecules, after impact and before, needs to be considered. This is admittedly a rather artificial assumption, but its treatment will be found of value in bringing out clearly the comparative applicability of the idea of regular reflection.

Case of Regular Reflection of the Ions.—For this case we need to consider only the component velocity of the ions normal to the equipotential surfaces, including the electrode. These we will assume to be parallel planes. Without making an appreciable error we may assume—for the highly conductive negative glow—that the entire applied P.D. is condensed in the polarization region of the transverse cathode, and that the flow into this region is by diffusion. This would at least be true for a vanishing value of j.

Let u_0 be the component temperature velocity with which those ions enter the polarization region which rebound with just sufficient velocity to carry them out again. Then similarly to (5)

$$V_b = \frac{1}{2} \cdot \frac{m}{e} \cdot \frac{1-k}{k} \cdot u_0^2, \tag{12}$$

where k represents now, as contrasted with k', the *real* fractional loss of energy by impact on the electrode. From this we obtain

$$k = \frac{\frac{1}{2} \cdot \frac{m}{e} \cdot u_0^2}{\frac{1}{2} \cdot \frac{m}{e} \cdot u_0^2 + V_b}. \tag{13}$$

The value of u_0 may be calculated from the temperature—assuming the entrant ions have the same mean kinetic energy as the gas molecules. Maxwell's law of velocity distribution gives

$$\frac{dn}{n} = \frac{4}{\pi^{3/2}} \cdot \frac{c^2}{\alpha^3} \cdot e^{-(c^2/\alpha^2)} \cdot dc, \tag{14}$$

where dn/n is the fractional number of the molecules whose speed is between c and $c + dc$; and α is the most probable speed of the n molecules. To obtain the corresponding fraction whose component velocity lies between u and $u + du$ we have from (14)

$$\frac{dn}{n} = \frac{1}{\pi^{3/2}\alpha^3} e^{-(u^2/\alpha^2)} du \int_{-\infty}^{\infty} e^{-(v^2/\alpha^2)} dv \int_{-\infty}^{\infty} e^{-(w^2/\alpha^2)} dw = \frac{1}{\sqrt{\pi}\alpha} \cdot e^{-(u^2/\alpha^2)} du. \tag{15}$$

Let now n'/n be the fractional number of those *entering* unit area of the polarization region, having a component velocity greater than u_0 as defined in (13). For this case dn/n is double the value given in (15), since there n would express those passing through unit area in both directions. We obtain by integration

$$\frac{n'}{n} = \frac{2}{\sqrt{\pi}} \int_{u_0/\alpha}^{\infty} e^{-(u/\alpha)^2} d\left(\frac{u}{\alpha}\right) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{u_0/\alpha} e^{-(u/\alpha)} d\left(\frac{u}{\alpha}\right). \tag{16}$$

We have calculated the values of u_0/α from (16), for various values of n'/n, by the aid of a table of definite integrals. These are given in Table II., which shows for example, that only about 15 per cent. of the molecules of a gas have a component velocity greater than α.

TABLE II.

n'/n.	u_0/α.	n'/n.	u_0/α.	n'/n.	u_0/α.	n'/n.	$u_0\alpha/$.
.10	1.16	.35	.66	.60	.37	.85	.13
.15	1.02	.40	.60	.65	.32	.90	.09
.20	.91	.45	.53	.70	.27	.95	.04
.25	.81	.50	.48	.75	.23		
.30	.73	.55	.42	.80	.18		

TABLE III.

$n'/n.$	$c_0/a.$	$n'/n.$	$c_0/a.$	$n'/n.$	$c_0/a.$	$n'/n.$	$c_0/a.$
1.000	.10	.90	.55	.66	.90	.34	1.30
.995	.20	.87	.60	.62	.95	.27	1.40
.99	.25	.84	.65	.57	1.00	.21	1.50
.97	.35	.81	.70	.54	1.05	.163	1.60
.96	.40	.77	.75	.49	1.10	.12	1.70
.94	.45	.735	.80	.45	1.15	.09	1.80
.92	.50	.695	.85	.41	1.20	.045	2.00

In Table III. are given a series of corresponding values for c_0/α calculated from (14). It shows for example that 57 per cent. of the molecules have a speed greater than α, while only 4.5 per cent. have a speed more than twice its value.

EXPERIMENTAL.

To test the above theory of the temperature effect, measurements have been made with transverse electrodes of aluminum, steel and platinum placed in the negative glow of a separate ionizing current through hydrogen. The apparatus was described in detail in the previous article.

A series of measurements consisted in observing the transverse current produced by various applied potentials between the transverse electrodes —with check readings made in all cases to insure against any progressive change. Table IV. gives a characteristic series from aluminum as cathode. The first two columns contain the observed magnitude of polarization P. D. and corresponding current density at the transverse cathode. The third column gives the calculated values of n'/n as obtained from (11) by assuming that n' vanishes at the higher potentials. This table shows that with a polarization P. D. of .46 volt 67 per cent. of the entrant ions according to the theory, escape without giving up their charge; while with a P. D. of 4.6 volts, 13.5 per cent. escape.

To calculate k—from (13)—it is necessary to obtain the value of $\frac{1}{2} \cdot (m/e) \cdot u_0^2$ in terms of the potential difference in volts required to produce it. We have

$$\frac{1}{2}\frac{m}{e}u_0^2 = \frac{1}{2}\frac{m}{e}\alpha^2\left(\frac{u_0}{\alpha}\right)^2.$$

For a hydrogen molecule at 20° C.—the assumed temperature of the negative glow[1]—

$$\alpha = 1.55 \times 10^5 \text{ cm./sec.}$$

If it carries a univalent charge

[1] Wood—Wied. Ann., 59, p. 238—did not find it much above room temperature.

$$\frac{m}{e} = .7 \times 10^{-14} \text{ c.g.s.e.s.}$$

Then

$$\frac{1}{2}\frac{m}{e}u_0^2 = .84 \times 10^{-4}\left(\frac{u_0}{\alpha}\right)^2 \text{ c.g.s.e.s.}$$

$$= 2.5 \times 10^{-2}\left(\frac{u_0}{\alpha}\right)^2 \text{ volts.} \qquad (17)$$

From (17) Table II., and (13) the values of k given in the fourth column of Table IV. were calculated. These show about one half per cent. loss of energy on impact, which is nearly the same for all polarizations between .46 and 4.6 volts. In the next column is given the calculated

TABLE IV.

Aluminum Cathode in Hydrogen.

Gas pressure: 1.48 mm. Ionizing Current: 1.10 m.a.

V_b (Volts).	j (M. A.).	n'/n.	k.	k_c.	V_b.	j.	n'/n.
.46	$.80\times10^{-2}$	.67	.0049	.042	14.3	13.7×10^{-2}	−.004
.92	1.56	.55	.0048	.029	19.2	15.8	.000
1.85	3.04	.38	.0052	.021	29.0	19.8	−.020
2.80	4.40	.27	.0054	.017	38.9	22.2	.010
3.75	5.44	.22	.0051	.015	48.8	24.8	.015
4.65	6.72	.135	.0060	.015	58.6	27.6	.000
9.45	11.0	.007	——	—	68.5	30.0	−.006

values of the loss by impact for the special form of reflection in which the speed c_0 is used in (13) instead of the component velocity u_0. This magnitude is found to vary nearly three times within the same range in which the value obtained from u_0 varies only about 20 per cent. Thus the results are found distinctly in favor of the theory of regular reflection. In the succeeding tables the constant for regular reflection only has been calculated.

Table V. gives the mean values obtained from four series of observations on aluminum cathodes—freshly cleaned, by filing, for each series—taken

TABLE V.

Aluminum Cathode in Hydrogen.

V_b.	n'/n.	k.	V_b.	n'/n.
.45	.675	.0048	14.1	−.025
.90	.555	.0048	19.0	−.03
1.82	.395	.0050	28.7	−.015
2.74	.28	.0053	38.6	.015
3.65	.205	.0055	48.4	.007
4.60	.135	.0061	58.2	.004
9.30	−.005	——	68.1	.002

with gas pressures from 1.5 to 2.0 mm., and with ionizing currents varying from 1.1 to 2.0 m.a. These different sets agreed very satisfactorily. This table brings out a slight increase in k with increasing polarization P. D., which appears consistent with the fact that k' in Table I. is about 2.5 per cent., while k in this table is only .5 per cent. If there were no change with polarization P. D. k' should be somewhat less than k instead of greater.

Table VI. gives likewise the means of three similar series of results with steel cathodes of the same dimensions as the aluminum—area: .25 cm².

TABLE VI.

Steel Cathode in Hydrogen.

V_b.	n'/n.	k.	V_b.	n'/n.
.46	.70	.0040	14.2	.085
.91	.58	.0042	19.1	.035
1.83	.43	.0043	38.8	.02
2.75	.32	.0044	38.6	.003
3.70	.245	.0045	48.5	−.002
4.60	.185	.0048	58.3	−.003
9.4	.09	——	68.2	−.01

For steel, as expected, k is somewhat smaller than for aluminum. It should be, however, in the same ratio to aluminum that is found from Table I. for k' but this is not the case. The ratio for k' is 1 : 2 while for k it is about 4 : 5. An explanation for this discrepancy is suggested by the results from platinum—given in Table VII.

TABLE VII.

Platinum Cathode in Hydrogen. Showing Gradual Change with Time in Service.

V_b.	A.		B.		C.		D.	
	n'/n.	k.	n'/n.	k.	n'/n.	k.	n'/n.	k.
.45	.735	.0033	.675	.0048	.665	.0052	.63	.0064
.90	.61	.0036	.58	.0042	.565	.0046	.485	.0068
1.80	.445	.0040	.40	.0050	.365	.0056	.31	.0071
2.70	.335	.0043	.29	.0051	.27	.0056	.20	.0077
3.65	.245	.0046	.20	.0057	.18	.0062	.125	.0082
4.55	.19	.0047	.14	.0060	.12	.0067	.07	
9.3	.06		.045		.015		−.005	
14.1	.018		.02		−.007		−.023	
19.0	.005		.005		.00		−.017	
28.7	.000		.01		−.005		.00	
38.5	.002		.00		.00		−.003	
48.4	−.005		.00		.00		.005	
58.2	.013		−.01		.003		.01	
68.1	−.015		.01		.00		.025	

The sequence of tests made with platinum are given under the columns *A*, *B*, *C*, *D*. These tests extended over three days' time, during which the platinum was kept in an atmosphere of hydrogen at low pressure. A progressive increase of k is clearly evident—supposedly due to a change in the metal surface arising from the absorption of hydrogen. Under ordinary cathode polarizations of say 140 volts or more, the hydrogen is probably kept expelled from the cathode surface by the resulting bombardment, while with the potentials of five volts and under this is probably not the case. The result is a somewhat different surface condition of the same metal under different polarizations.

Discussion.—We have found that, under the assumption of no appreciable collisions between the discharging ions in the polarization region, they must suffer regular reflection at the cathode. Considering the relative irregularities of the electrode surface, regular reflection seems impossible.

If, however, the reflection be diffuse, then the collisions between the ions within the polarization region must be sufficiently numerous to produce a resultant velocity distribution approximately satisfying Maxwell's law. The " temperature " of the ions at a given equipotential surface would then be less than at the electrode by an amount determined by their stored up potential energy, relative to that at the electrode surface. Thus we should have a velocity distribution at the outer boundary of the polarization region, for the rebounding ions, similar to that for the entrant ions—except that the average velocity of the latter would be higher, and therefore a greater number entering than escaping.

This view probably accounts for the apparent applicability of the theory of a regular reflection of the ions impinging on the cathode. If it be correct then k' derived from the mean conditions should, like k, represent the average loss of energy of the ions which get back to the outer boundary of the polarization region.

THE BRACE LABORATORY,
UNIVERSITY OF NEBRASKA,
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CRITICAL EXAMINATION OF THE LAW OF X-RAY LINE SPECTRA.

BY HORACE SCUDDER UHLER.

THE present paper differs from my earlier one[1] on the same subject in three respects: (i) It includes the wave-lengths of all the accurately measured lines of the K-series (only a few of which were formerly accessible to me), (ii) it contains the results of more rigorous calculations, and (iii) it presents the material in greater detail. The object of the paper is to subject to critical examination the functional dependence of the X-ray lines of any one sub-series upon the corresponding atomic numbers so that answers may be given to the following questions, which are: How accurately does Moseley's law reproduce the observed wave-lengths? What other empirical formula will represent the numerical data within the given limits of experimental error? And what is the probable order of magnitude of the high frequency radiations of elements having small atomic numbers and of which the spectra have not yet been obtained? All the wave-lengths used (save two) may be found in a paper[2] by M. Siegbahn entitled "Bericht über die Röntgenspektren der chemischen Elemente (Experimentelle Methoden und Ergebnisse)." These data were chosen because they are the most recent, they were all obtained in the same laboratory with the same spectrometers, and they constitute the most extensive, accurate, and consistent set available.

In Moseley's second paper[3] the analytical result of his investigations is concisely stated in the sentence: "From the approximate linear relation between $\nu^{1/2}$ and N for each line we obtain the general equation $\nu = A(N - b)^2$, where A and b are constants characteristic of each line." That b may not equal zéro is pointed out very clearly in Moseley's reply[4] to certain objections raised by F. A. Lindemann. Accordingly, in the present paper, the equation $\sqrt{\nu_N} = a + bN$ will be referred to as Moseley's law. The degree of accuracy with which this relation represents the experimental wave-lengths will now be considered.

[1] Proc. Natl. Acad., Vol. 3, p. 88, Feb., 1917.
[2] Jahrbuch der Radioaktivität und Elektronik, Vol. 13, Part 3, Sept., 1916.
[3] Phil. Mag., Vol. 27, p. 712, April, 1914.
[4] Nature, Vol. 92, p. 554, Jan. 15, 1914.

The values of the parameters a and b were calculated, by the method of least squares, from the square-roots of the reciprocals of the known wave-lengths (expressed in angstroms) and the corresponding atomic numbers, N. Then, from a, b, and N, the wave-lengths were recalculated.

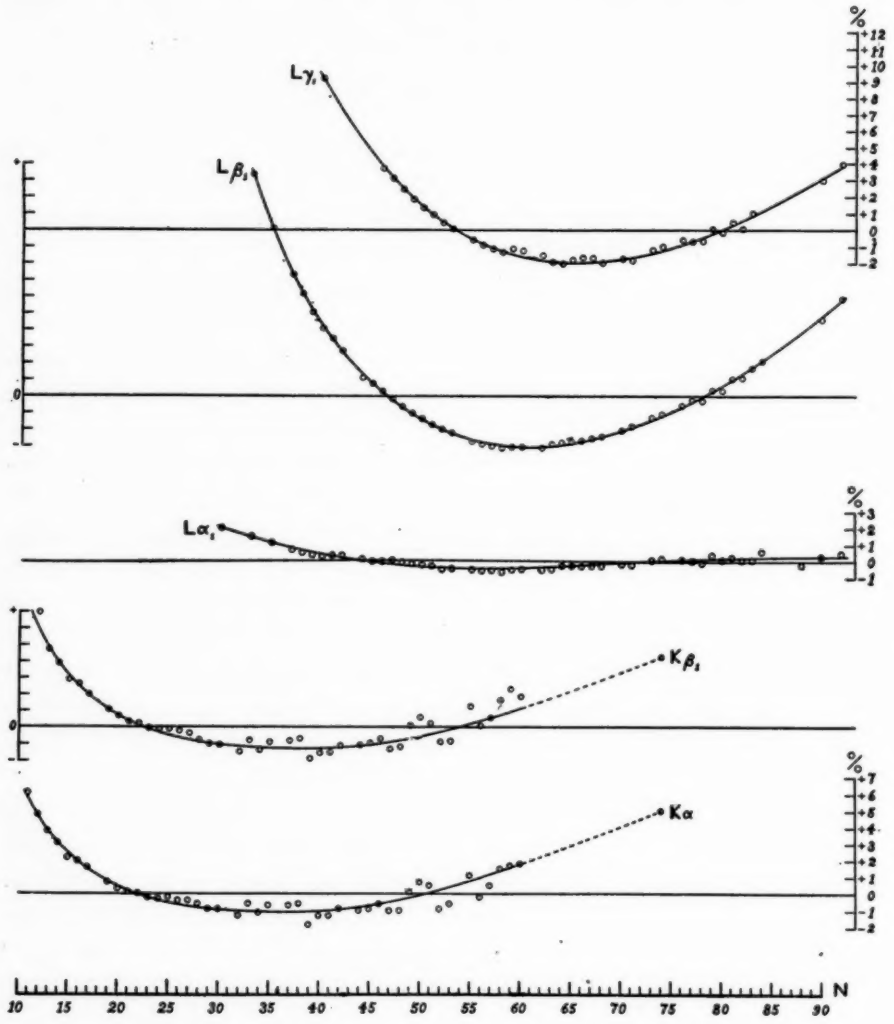


Fig. 1.

Finally the percentages by which the mathematical wave-lengths are algebraically greater than the experimental data were computed. This procedure was followed for the entire experimental range of each of the series K-α_m, K-β_1, L-α_1, L-β_1, and L-γ_1. Since some of the lines of the K-α series have not been measurably resolved into the two components

α_1 and α_2, mean values were used for all of the resolved pairs. For this reason the subscript m is written below the first α. The results obtained are shown graphically for five series in Fig. 1, and numerically for the K-α_m and L-β_1 series in the columns headed %, M of Tables I and II. The ordinates (with respect to the corresponding horizontal axes) of the centers of the little circles in the figure are the percentage deviations defined above, the common scale of the diagrams being indicated on the associated vertical axes. The abscissæ of these centers, which represent the atomic numbers, have their scale indicated at the bottom of the figure. The curves drawn through the five sets of points were not obtained by calculation since they are only intended to afford general guides to the eye. The two points at the extreme right ends of the curves for the K series were plotted from wave-lengths for tungsten, kindly furnished by A. W. Hull in a private communication. These data were not used in computing the values of the parameters a and b of Moseley's formula. For this reason the curves are indicated by short dashes from $N = 60$ to $N = 74$. Notwithstanding the fact that there is much room for improvement in the portions of the curves pertaining to values of N greater than 50 (especially for K-β_1), nevertheless the two points for tungsten seem to accord very well with the general drift of the nearer points which were derived from Siegbahn's tables. Incidentally, the circles for the K-α_m and K-β_1 series show (with the single exception for $N = 59$) precisely the same irregularities of distribution or "accidental" errors. This may indicate that homologous wave-lengths were derived from the same spectrograms and were dependent upon some poorly determined reference line, such as the direct image, for example.

Even a casual inspection of the five graphs brings out the fact that, in general, Moseley's law does not represent at all well the experimental data throughout the entire ranges now at our disposal. The percentage deviations at the extreme points and at the algebraic minima being respectively about + 6, + 5, − 1; + 7, + 4, − 1.2; + 2, + 0.2, − 0.6; + 13.3, + 5.8, − 3; and + 9.2, + 4, − 2; for the K-α_m, K-β_1, L-α_1, L-β_1, and L-γ_1 series. Most of these deviations greatly exceed the experimental errors estimated by the original investigators. For the K series, from germanium to chromium, it is stated[1] that: "The agreement of the lines measured on different plates is very good; the deviations are of the order of magnitude of 0.1 to 0.2 per cent." For the L series, from tantalum to uranium, it is remarked[2] that: "The accuracy of the

[1] Physikal. Ztschr., p. 48, Feb. 15, 1916.
[2] Phil. Mag., Vol. 32, p. 41, July, 1916.

measurements is estimated to about 0.3 per cent." With regard to the L series, from zinc to lutetium, the author says:[1] "The reflexion angles calculated have an uncertainty of about 0.3 per cent." Unfortunately I have not been able to find data of this kind for the remaining wave-lengths in Siegbahn's list. Hull's values for tungsten, which were obtained by the ionization method, are probably not in error by more than one per cent. Another fact brought out by the graphs is that Moseley's law represents the L-α_1 series better than any of the remaining four. This is quite contrary to all the accessible statements in the literature of the subject since they consistently convey the impression that Moseley's law holds very well for the K series but that it needs correction in the region of shortest wave-lengths of the L series. In fact, O. W. Richardson exceeds the original qualifying remarks of Moseley when he says:[2] "For the K series the agreement is quite exact, but for the L series there is a slight deviation from linearity with the elements of very high atomic weight." Since the preceding examination shows conclusively that Moseley's law (as distinguished from his epoch-making association of the chemical elements with atomic numbers and broad point of view) does not satisfactorily represent the experimental wave-lengths over the entire ranges of the five longest sub-series, the next problem is to find a function which will reproduce the numerical data within the estimated limits of experimental error.

The only interpolation formula which I have been able to find in the literature is the one proposed by A. W. Hull.[3] For the K series he gives $\nu_\alpha = 1.64 \times 10^{15} N^{2.10}$ and $\nu_\beta = 1.56 \times 10^{15} N^{2.15}$, true frequencies being represented. Since the exponents of N do not seem to be promising from the theoretical standpoint, as their values were obtained by the graphical method alone, and since the formula was not given the more crucial test of the L series, I have not subjected it to examination by the method of least squares. On the other hand, Hull's function has at least one desirable property, that is, simplicity.

Since last fall I have tested the equation[1]

$$\sqrt{\nu_N} = A + BN + \frac{C}{D - N} \qquad (1)$$

fairly exhaustively without succeeding either in replacing it by a function involving less than four parameters or in finding any systematic deviation between the wave-lengths computed from it and the experimental data. Any true but slight discordance may, of course, be masked by the

[1] Phil. Mag., Vol. 32, p. 497, Nov., 1916.

[2] "The Electron Theory of Matter," p. 511, 1914.

[3] Proc. Natl. Acad., Vol. 2, p. 267, May, 1916.

inaccuracies in the observed quantities, which is a question that future investigation alone can decide. The particular form of equation (1) was found in the following empirical manner. The residuals of $\sqrt{\nu_N}$ (not percentage deviations of wave-lengths), obtained by applying the method of least squares to Moseley's law, were plotted on a large scale in the hope of obtaining a correction "term" to the linear relation. Inspection of the five sets of points thus obtained suggested that the hyperbola $c_0N^2 + Nr + c_1N + c_2r + c_3 = 0$ ($r \equiv$ residual) would fulfil the requirements of the problem. As stated above, subsequent rigorous calculations have confirmed this belief. The correction expression may be transformed into

$$-r = a' + c_0N + \frac{C}{D - N},$$

where $a' = c_1 - c_0c_2$, $C = c_2(c_1 - c_0c_2) - c_3$, and $D = -c_2$. Since $\sqrt{\nu_N} = a + bN - r$ the final form is equation (1), where $A = a + a'$, and $B = b + c_0$. Since equation (1) may be written $BN^2 - N\sqrt{\nu_N} + (A - BD)N + D\sqrt{\nu_N} - (C + AD) = 0$ the geometric meaning of the new formula is that the square-roots of the frequencies of the X-ray lines are related to the atomic numbers in the same way as the ordinates and absicssæ of the points on an hyperbola. In short, these radicals form a family of hyperbolæ for the five series tested. This result was brought out by the magnification of which the residuals were susceptible, but it could not have been seen so readily by plotting $\sqrt{\nu_N}$ against N directly. See, for example, the approximate straight lines given by Moseley, Siegbahn, and others.

The wave-lengths calculated by the aid of formula (1) and the percentage deviations of the numbers thus obtained are given in the columns headed λ_c, U and %, U, respectively, in Tables I and II. The series K-α_m and K-β_1 were selected as typical since the shorter wave-lengths of the former seem to involve relatively large experimental errors while those of the latter appear to constitute the most accurate set of all. For the same reasons the correction coefficients c_0, c_1, c_2, c_3 were obtained graphically for the K-α_m series, and by the method of least squares for the L-β_1 lines. In fact, as might be expected, in the cases where both methods were applied to one and the same series the gain in accuracy attained by the more rigorous computation was slight and altogether incommensurate to the extra labor entailed. The probable errors of a single residual, expressed in per cent., are $\pm$ 0.28, $\pm$ 0.25, $\pm$ 0.11, $\pm$ 0.10, and $\pm$ 0.16 for the K-α_m, K-β_1, L-α_1, L-β_1, and L-γ_1 series, in the order named. It is therefore clear that equation (1) represents the

TABLE I.

Series K-α_m.

El.	*N.*	λ_c.	λ_c, *M.*	λ_c, *U.*	%, *M.*	%, *U.*
W.....	74	0.210	0.220	0.210	+5.0	0.0
Nd.....	60	0.333	0.338	0.334	+1.8	+0.3
Pr.....	59	0.345	0.350	0.346	+1.7	+0.4
Ce.....	58	0.358	0.363	0.359	+1.5	+0.4
La.....	57	0.374	0.376	0.373	+0.5	−0.4
Ba.....	56	0.391	0.390	0.387	−0.2	−0.9
Cs.....	55	0.400	0.405	0.402	+1.1	+0.5
I.....	53	0.439	0.437	0.435	−0.6	−0.9
Te.....	52	0.458	0.454	0.453	−0.9	−1.0
Sb.....	51	0.470	0.472	0.472	+0.5	+0.5
Sn.....	50	0.489	0.492	0.493	+0.7	+0.8
In.....	49	0.513	0.513	0.514	+0.1	+0.3
Cd.....	48	0.541	0.535	0.537	−1.0	−0.7
Ag.....	47	0.565	0.559	0.561	−1.0	−0.6
Pd.....	46	0.588	0.584	0.587	−0.6	−0.1
Rh.....	45	0.617	0.612	0.615	−0.9	−0.3
Ru.....	44	0.647	0.641	0.645	−1.0	−0.3
Mo.....	42	0.712	0.705	0.711	−0.9	−0.1
Nb.....	41	0.752	0.741	0.748	−1.3	−0.5
Zr.....	40	0.791	0.780	0.788	−1.3	−0.3
Y.....	39	0.838	0.822	0.831	−1.8	−0.8
Sr.....	38	0.874	0.868	0.877	−0.6	+0.4
Rb.....	37	0.924	0.918	0.927	−0.7	+0.4
Br.....	35	1.038	1.030	1.042	−0.7	+0.4
Se.....	34	1.107	1.094	1.107	−1.1	0.0
As.....	33	1.172	1.165	1.178	−0.6	+0.5
Ge.....	32	1.259	1.242	1.256	−1.3	−0.2
Zn.....	30	1.435	1.422	1.437	−0.9	+0.1
Cu.....	29	1.541	1.527	1.542	−0.9	+0.1
Ni.....	28	1.655	1.645	1.660	−0.6	+0.3
Co.....	27	1.783	1.776	1.791	−0.4	+0.4
Fe.....	26	1.930	1.923	1.937	−0.4	+0.4
Mn.....	25	2.095	2.090	2.103	−0.2	+0.4
Cr.....	24	2.286	2.279	2.290	−0.3	+0.2
V.....	23	2.500	2.495	2.503	−0.2	+0.1
Ti.....	22	2.744	2.744	2.747	0.0	+0.1
Sc.....	21	3.030	3.032	3.029	+0.1	0.0
Ca.....	20	3.357	3.367	3.355	+0.3	−0.1
K.....	19	3.737	3.761	3.737	+0.7	0.0
Cl.....	17	4.712	4.790	4.723	+1.6	+0.2
S.....	16	5.360	5.470	5.369	+2.0	+0.2
P.....	15	6.168	6.306	6.155	+2.2	−0.2
Si.....	14	7.131	7.349	7.127	+3.1	−0.1
Al.....	13	8.360	8.675	8.347	+3.8	−0.2
Mg.....	12	9.915	10.394	9.909	+4.8	−0.1
Na.....	11	11.951	12.681	11.951	+6.1	0.0

Table II.

Series L-β_1.

El.	*N.*	λ_e.	λ_c, *M.*	λ_c, *U.*	%, *M.*	%, *U.*
U.....	92	0.720	0.762	0.719	+ 5.84	−0.11
Th.....	90	0.766	0.801	0.764	+ 4.62	−0.22
Po.....	84	0.920	0.940	0.921	+ 2.13	+0.11
Bi.....	83	0.950	0.966	0.951	+ 1.69	+0.08
Pb.....	82	0.983	0.994	0.982	+ 1.09	−0.13
Tl.....	81	1.012	1.023	1.014	+ 1.04	+0.19
Hg.....	80	1.049	1.053	1.047	+ 0.35	−0.15
Au.....	79	1.080	1.084	1.082	+ 0.38	+0.21
Pt.....	78	1.120	1.117	1.119	− 0.28	−0.12
Ir.....	77	1.154	1.151	1.157	− 0.23	+0.23
Os.....	76	1.194	1.187	1.196	− 0.56	+0.19
W.....	74	1.278	1.265	1.281	− 1.05	+0.22
Ta.....	73	1.323	1.306	1.326	− 1.28	+0.23
Lu.....	71	1.421	1.395	1.423	− 1.80	+0.12
Yb.....	70	1.474	1.444	1.475	− 2.07	+0.04
Er.....	68	1.586	1.548	1.586	− 2.42	0.00
Ho.....	67	1.646	1.604	1.646	− 2.56	−0.01
Dy.....	66	1.709	1.663	1.709	− 2.67	−0.01
Tb.....	65	1.775	1.726	1.775	− 2.75	0.00
Gd.....	64	1.844	1.793	1.845	− 2.79	+0.04
Eu.....	63	1.918	1.863	1.918	− 2.87	+0.01
Sa.....	62	2.000	1.937	1.996	− 3.13	−0.21
Nd.....	60	2.167	2.101	2.164	− 3.06	−0.14
Pr.....	59	2.259	2.190	2.255	− 3.05	−0.16
Ce.....	58	2.359	2.285	2.352	− 3.12	−0.28
La.....	57	2.461	2.387	2.455	− 3.00	−0.25
Ba.....	56	2.569	2.496	2.564	− 2.86	−0.20
Cs.....	55	2.684	2.612	2.680	− 2.69	−0.16
I.....	53	2.934	2.870	2.934	− 2.19	0.00
Te.....	52	3.074	3.013	3.074	− 1.97	0.00
Sb.....	51	3.222	3.168	3.223	− 1.67	+0.04
Sn.....	50	3.381	3.335	3.383	− 1.36	+0.06
In.....	49	3.550	3.515	3.554	− 0.98	+0.13
Cd.....	48	3.733	3.711	3.738	− 0.59	+0.14
Ag.....	47	3.929	3.923	3.936	− 0.15	+0.17
Pd.....	46	4.142	4.154	4.148	+ 0.29	+0.15
Rh.....	45	4.372	4.406	4.378	+ 0.78	+0.13
Ru.....	44	4.630	4.682	4.625	+ 1.12	−0.10
Mo.....	42	5.175	5.317	5.185	+ 2.74	+0.19
Nb.....	41	5.493	5.684	5.502	+ 3.47	+0.16
Zr.....	40	5.851	6.090	5.847	+ 4.08	−0.07
Y.....	39	6.227	6.542	6.224	+ 5.05	−0.04
Sr.....	38	6.639	7.045	6.638	+ 6.12	−0.02
Rb.....	37	7.091	7.610	7.092	+ 7.31	+0.02
Br.....	35	8.141	8.962	8.146	+10.09	+0.07
As.....	33	9.449	10.710	9.445	+13.35	−0.04

chosen data very satisfactorily and that it will be found very reliable for interpolation, and for extrapolation over a short range of atomic numbers. To facilitate such calculations the numerical values of A, B, C, and D are given in Table III. The column headed "Range" contains the extreme values of N used in calculating these four coefficients.

In using this table two facts should be noted: (i) Siegbahn used the grating space $d = 2.814 \times 10^{-8}$ cm. for rock salt, and $d = 7.621 \times 10^{-8}$ cm. for gypsum; and (ii) the values of λ_N resulting from the use of equation (1) and the tabulated numerical coefficients will be expressed in angstroms.

TABLE III.

Series.	A.	B.	C.	D.	Range.
K-α.....	−0.18724	+0.026898	+ 21.74629	+131.388*	11–74
K-β_1.....	−0.44795	+0.027774	+ 69.60474	+170.987	12–74
L-α_1.....	−0.55066	+0.013658	−108.60609	−225.000*	30–92
L-β_1.....	−0.43675	+0.009386	+ 66.94285	+180.973	33–92
L-γ_1.....	−0.26791	+0.012837	+ 19.38426	+145.197	40–92

* Obtained by graphical treatment of *residuals*.

Before passing to the question of extrapolating to $N = 1$ it may not be superfluous to call attention to the following points. In the first place, with the exception of the top number, the values of D in Table III are approximately integers. Undoubtedly these constants may be replaced by the nearest integers without sensibly decreasing the present accuracy of fit of equation (1), it being at most necessary to apply small corrections to the associated values of A, B, and C. Since slight changes in the experimental data exert an appreciable influence on D, and as the value of this constant is very close to an integer for the series L-β_1 (− 0.015 per cent. error), the wave-lengths of which seem to be affected by the smallest accidental errors, I am still[1] of the opinion that, if the correct formula for X-ray line series, when found, contains a binomial of the type $(D - N)^{-n}$, D will be exactly a whole number; signifying, perhaps, a physical change in origin for N. If this be true, it might be desirable to express ν_N as a function of $D - N$ instead of N alone. In the second place, realizing that equation (1) possesses the undesirable feature of involving four parameters I tried the formulæ $\nu_N = a + b(c + N)^{-1}$ and $\nu_N = a' + b'(c' + N)^{-2}$ which were suggested by the expression obtained by squaring equation (1). It was found that both of the functions just given are altogether unsatisfactory.

An attempt will now be made to arrive at a necessarily tentative answer to the third question proposed in the first paragraph of this paper.

The problem is to determine the order of magnitude of the X-ray lines of hydrogen by making use only of wave-lengths of the same series and purposely avoiding the introduction of any auxiliary theoretical assumptions. By plotting, on a large scale, atomic numbers and wave-lengths as abscissæ and ordinates respectively it becomes apparent at once that the loci of the five longest series approach the axis of ordinates very gradually as the atomic numbers decrease. Accordingly the wave-lengths deduced for hydrogen may be expected to depend to an undesirable degree upon the particular form of function employed for extrapolation. Especial care must therefore be taken to choose an algebraic expression which will implicitly influence the results to as slight an extent as possible. In spite of the fact that the K-α_m series only has to be extrapolated from $N = 11$ to $N = 1$, neither the linear law nor equation (1) will suffice. Moseley[3] assigns to b [$\nu_N = A(N - b)^2$] the values 1 and 7.4 for the "$K\alpha$ line" and the "$K\beta$ line," respectively. Hence, his formula leads to an infinite wave-length for the K-α_m line of hydrogen. For the K-β_1 series the same equation causes λ_N to increase as N decreases from 11 to 8, to become infinite for $N = 7.4$, and to decrease when N continues from 7 to 1. Siegbahn[6] writes the law in question as $\sqrt{\nu} = a(N - N_0)$, and finds that the values of N_0 are 6.97, 6.09, and 9.92 for the interval Ta to U of the α_1, α_2, and β_2 sub-series of the L group. Equation (1) exhibits the same peculiarity, the right member vanishing when N equals 1.35, 5.88, 11.54, and 9.72 for the series K-β_1, L-α_1, L-β_1, and L-γ_1, respectively. For the K-α_m series and $N = 1$ it leads to the relatively enormous wave-length 2.42 μ. A variety of explanations of these apparent anomalies suggest themselves at once. (*a*) The elements of small atomic number may not radiate the K and L series. This idea is consistent with the fact that the M series has only been found for the elements of high atomic number (79 to 92) from gold to uranium. (*b*) The X-ray wave-lengths may pass through arithmetical maxima and then decrease. This would be somewhat analogous to the correlation of the lines of certain principal series in the visible and infra-red regions of the spectrum which correspond to negative values of the frequency in the formula of Ritz. (*c*) The concordance of formula (1) with the experimental data may be illusory. Although the third suggestion may be the correct one it seems fair to call attention to the fact that the errors involved in the given wave-lengths (especially for the elements of high atomic number) exert an appreciable influence on the values of the parameters A, B, C, and D. Thus, for the K-α_m series, substitution of $N = 1$ in equation (1) leads to $\sqrt{\nu_1} = -0.1872 + 0.0269 + 0.1668 = 0.0065$ or $\nu_1 = 0.000042$.

Slight changes in the coefficients would therefore produce a very great alteration in the wave-length obtained from $\sqrt{\nu_1} = A + B + C(D-1)^{-1}$.

The least objectionable way of extrapolating is to apply the method of least squares to the computation of the coefficients of a sufficient number of terms of the power polynomial $\nu_N = a_0 + a_1N + a_2N^2 + \cdots + a_kN^k$, care being taken to use about fifteen of the largest wave-lengths. An inspection of the left ends of the five curves of Fig. 1, or reference to the original papers, will show that the data in these regions are fortunately the most accurate. Using only the first three terms of the polynomial and then putting $N = 1$ leads to 366 Å., 95 Å., and 22 Å. respectively, for the series K-α_m, L-α_1, and L-β_1. Four terms give 130 Å. and 49 Å. for K-α_m and L-β_1. The corresponding values of a_3 were $-$ 0.000000698 and $+$ 0.000000320, and hence further calculations were omitted as superfluous. Accordingly, the evidence obtained solely from the experimental wave-lengths leads to the tentative conclusion that the X-ray lines for all the elements will have wave-lengths inferior to 510 Å., which is the limit last attained by Lyman. Incidentally it may be noted that, for the L-β_1 series, extrapolation to $N = 92$ (uranium) by aid of the cubic (a_0, a_1, a_2, a_3) gives an error of $+$ 9.6 per cent. in the calculated wave-length. Therefore, the close fit of formula (1) cannot be due entirely to the fact that it involves four independent parameters.

In conclusion four sentences in Moseley's second paper[3] will be quoted for reasons which will appear later. "On this principle the integer N for *Al*, the thirteenth element, has been taken to be 13, and the values of N then assumed by the other elements are given on the left-hand side of Fig. 3. This proceeding is justified by the fact that it introduces perfect regularity into the X-ray spectra." "Now if either the elements were not characterized by these integers, or any mistake had been made in the order chosen or in the number of places left for unknown elements, these regularities would at once disappear. We can therefore conclude from the evidence of the X-ray spectra alone, without using any theory of atomic structure, that these integers are really characteristic of the elements." The point to be brought out is that the last sentence must not be taken so literally as to mean that the X-ray data alone necessitate associating the integers 1, 2, ···, 13, ···, 74, ···, 92 with H, He, ···, Al, ···, W, ···, U, respectively; for, the "regularities" will not disappear if the coördinate plane be expanded or contracted parallel to the axis of N. More specifically, as far as the X-ray data are concerned, the atomic numbers need not be integral and they do not have to form an arithmetical progression explicitly.[1] In fact, in making the computa-

[1] The discrete values of log N, say, may be taken as a new sequence of atomic numbers, thus involving the accepted series implicitly.

tions I shifted the origin to the "center of gravity" of the N sequence, divided by 10, etc. These comments would be highly pedantic and irrelevant if removed from the following remarks. The facts that equation (1) leads to infinite wave-lengths for values of N appreciably greater than unity, that the M series has only been excited in the heaviest elements, and that—as Siegbahn points out—the intensities of the lines of any one sub-series decrease, on the whole, and finally vanish (experimentally) as the atomic number becomes smaller, suggest that the mechanisms which give rise to these radiations may cease to function or even to exist (loss of outer rings of electrons) for definite values of N. In short, if it should ever become desirable, for theoretical or other reasons, to use different sets of atomic numbers for the K, L, and M series the transformation of coördinates would not disturb the fundamentally important regularities discovered by Moseley.

SUMMARY.

1. It is shown that Moseley's law, $\nu = A(N - b)^2$, does not satisfactorily represent the X-ray series over the entire ranges of wave-lengths now known.

2. The formula $\nu^{1/2} = A + BN + C(D - N)^{-1}$—where A, B, C, and D are constants for any one sub-series—is proposed and shown to reproduce the observed data within the given limits of experimental error.

3. The uncertainty pertaining to extrapolation of the series as far as hydrogen is discussed. The tentative conclusion is reached that the X-ray lines of hydrogen, if they exist, probably have wave-lengths less than about 400 angstroms.

4. Attention is called to the fact that the series of natural numbers commencing with 1 is not the only arithmetical progression which may be used as the sequence of atomic numbers consistent with Moseley's "regularities."

SLOANE PHYSICAL LABORATORY,
YALE UNIVERSITY,
February 1, 1917.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

ON SOME VERY LARGE VARIATIONS IN THE ADSORPTION OF CERTAIN SPECIMENS OF CHARCOAL.[1]

BY HARVEY B. LEMON.

A PRELIMINARY report given at the November meeting a year ago indicated that among samples of charcoal great differences in the adsorptive power existed which could be associated with the temperature of carbonization of the cocoanut shell, 825° to 875° C. being given as the range within which samples passed from the condition of being good adsorbers to that of being very poor ones.

Subsequent work has shown further that a single specimen can be made to show all of the variations previously observed among different specimens. All samples consistently improve with use, *i. e.*, with repeated "outgassing-heating" and adsorption, provided the former is not carried on at too high a temperature. A sample which is quite poor, requiring over two hours to do a given task, (25 gm. adsorbing 1 liter air) with frequent testing becomes very good, *i. e.*, will do the same in less than one minute. During this process a certain characteristic cycle of curves [log pressure = F (log time)] is traversed, representing the behavior of successive tests.

Furthermore a good specimen may be ruined, even although repeatedly used, provided the outgassing-heating temperature is increased on successive runs. At any stage in the process however the specimen may be restored in whole or in part. With certain limitations, such a reversal of operations at any point does not interfere with subsequent progress in the initial direction. In all these experiments the same cycle of curves mentioned in the preceding paragraph is found, the family here being developed in the opposite order. Considerable further investigation will be needed before these phenomena can be interpreted with certainty.

Phenomena of quite a different type have been also observed, but merely in a qualitative manner. When charcoal is evacuated the gas is not given off at a uniformly increasing rate as the temperature is raised but comes off in great quantities at certain critical temperatures. Five minutes pumping at certain

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

temperatures may result in getting out more gas than would be obtained in five hours, thirty degrees lower. Spectroscopic observations show N_2 comes out freely at temperatures as low as 150°, the rush of O_2 begins at 300° and is greatly augmented again at 600°. Notable is the extremely high temperature 750° to 800° before H_2 makes a conspicuous appearance in the spectrum. At 900° H_2 dominates. For quantitative results experiments on pure gases are in progress.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
November 10, 1916.

PRELIMINARY NOTES ON THE TORSIONAL ELASTICITY OF DRAWN TUNGSTEN WIRES.[1]

BY L. P. SIEG.

PRELIMINARY experiments have been made on drawn tungsten wires, ranging in diameter from 0.099 cm. to 0.510 cm. for the determination of the coefficient of simple rigidity. The following is a summary of results:

1. For amplitudes well within the elastic limit the period varies with the amplitude, the variation being as great as 7.6 per cent.

2. The logarithmic decrement varies with the amplitude.

3. Statistically determined the torsional stress is proportional to the torsional strain within the limits in 1 above.

4. The coefficient of simple rigidity varies from 9.88 to 18.95 times 10^{11} dynes per cm^2. This is the largest rigidity that can be found in the literature, being in its largest values nearly two and one half times as great as that of steel.

5. The coefficient has been determined statically, and found to range from 9.08 to 17.28 $\times$ 10^{11} dynes per cm^2. These latter values are found uniformly smaller than the corresponding values kinetically determined.

6. The range in values for the rigidity is nearly 100 per cent. This does not equal the range in values in cadmium, and in lead[2] which is about 140 per cent.

7. The increase in the coefficient does not change in any regular manner with the change in size of the wire. Therefore new wires are to be used that are all definitely drawn from the same original lug. The present wires were chosen at random, and it is not at all certain that they were drawn from the same original piece.

8. With any given wire the results for the elasticity are remarkably constant, being only slightly affected by fatigue, and by a variation in the period of vibration.

Acknowledgment is made to the Nela Laboratory and to Dr. Worthing for their kindness in supplying the wires.

STATE UNIVERSITY OF IOWA,
November 15, 1916.

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

[2] See Winkelmann's Handbuch der Physik, Vol. 1, p. 652.

THE INTENSITY FACTOR IN BINAURAL LOCALIZATION AND AN EXTENSION OF WEBER'S LAW.[1]

BY G. W. STEWART AND O. HOVDA.

THE object of this experimental study was to isolate and to study the intensity factor when a pure tone is used. The actual ratio of intensities at the ears, using a frequency of 256 d.v., required to give a certain angular displacement in localization is ascertained.

It is found that if the intensity ratio is one to ten, then the displacement is 45 degrees from the median plane and on the side of the greater intensity. It is shown that, with a single source of sound about the head, this ratio of intensities with this frequency can but seldom occur in practice.

With such a single source at a distance of five meters, the intensity ratio at the ears does not exceed 1.2. The conclusion is that the intensity factor, when a pure tone is used, is very small.

The data obtained show clearly that the response (in the form of an angular displacement in localization) is proportional to the logarithm of the actual intensity ratio. This is a very interesting extension of Weber's Law.

STATE UNIVERSITY OF IOWA,
November, 1916.

AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF BINAURAL BEATS.[1]

BY G. W. STEWART.

BINAURAL beats, occurring when two sources varying slightly in frequency are presented one to each ear, can be considered under three heads, primary maxima and minima, secondary maxima and localization. The primary maxima and minima (intensities) occur at phase differences of 0° and 180° respectively, but the minima are not zero. The secondary maxima occur at phase differences of $180° - \delta$ and $180° + \delta$. (See abstract, PHYS. REV., Series 2, 3, p. 146, 1914.) The localization is external and in front for 0° phase difference, it wanders about the head on the side of the greater frequency for phase differences from 0° to $180° - \delta$ at which phase it is in the ear, it is then internal, crossing the head, until the phase difference is $180° + \delta$, when it is in the other ear. From $180° + \delta$ to 360° the localization is on the side of the less frequency, wandering from the right ear toward the front. The author seeks an explanation upon physical grounds.

It is shown that skull conduction will explain the primary maxima and minima with more than one assumption as to what causes the response. The two assumptions tried are that the organ responds to intensity and that it responds to the absolute value of the displacement.

The secondary maxima is explained by the assumption of a second pair of

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

organs which are independent of the first pair, and the assumption that there is a change of phase of 180° introduced in skull conduction.

The assumption of the two pairs of organs gives an explanation of all the intensity and localization phenomena observed. There appear to be no objections to the assumption from either an anatomical or physiological viewpoint.

STATE UNIVERSITY OF IOWA,
November, 1916.

SOME EFFECTS OF CROSS-MAGNETIZING FIELDS UPON HYSTERESIS.[1]

BY N. H. WILLIAMS.

THE effect of an alternating field applied at right angles to the direct field while the hysteresis curve was being traced has been investigated for steel specimens of varying degrees of hardness. The direct field reached a magnitude of 150 gauss while an alternating field of maximum intensity, 80 gauss, was applied in some cases. With soft specimens, all traces of hysteresis disappeared, while with very hard steel it was reduced till the width of the curve was less than a tenth of the width of the original curve.

For soft specimens, the magnetization curve with the alternating field applied lies almost wholly outside and beneath the normal hysteresis curve. For hard steel it lies within the normal curve, except near the top, where it passes outside and above it.

It has been possible to compute the induction that should correspond to any field intensity, and points thus determined are found to lie very near to the experimental curve. Their slight deviation from the experimental curve point to two conclusions: (1) The observed effects are not due to mechanical shock, as has been supposed by some. (2) With hard specimens there is a distinct rotational hysteresis or tendency for a flux to maintain its magnitude as it is forced to change its direction.

UNIVERSITY OF MICHIGAN,
November, 1916.

AN ACOUSTICAL THERMOMETER.[1]

BY F. R. WATSON AND H. T. BOOTH.

TEMPERATURE may be measured by the variation of a physical property of a substance with the temperature. As common examples, we have the mercury thermometer, the gas thermometer, the resistance thermometer, thermocouples and radiation pyrometers, which involve the properties of expansion, resistance, thermo-electricity, and radiation. In addition to these, the velocity of sound is shown theoretically to vary with the temperature. Thus

$$V_t = V_0 \sqrt{1 + \alpha t} = V_0 \sqrt{\frac{\theta}{273}},$$

[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

where V_t and V_0 are the velocities of sound at $t°$ C. and 0° C. respectively and θ is the absolute temperature. Combining this with $V = N\lambda$, where N is the pitch and λ the wave-length, we get

$$N^2 = \frac{V_0^2}{\lambda^2 273} \cdot \theta = \text{constant} \times \theta, \text{ if } \lambda \text{ is constant.}$$

Therefore $N^2 \propto \theta$.

This theory was tested experimentally in the present investigation, the pitch being found for a cylindrical resonator of constant length when it was heated to different temperatures. The cylindrical resonator was arranged as a Rayleigh resonator[1] with a flat, circular disc suspended at a loop 1/3 of the length of the tube from the closed end. This meant that the tube responded to its first overtone and its length, l, was equal to $3/4\,\lambda$. When the suspended disc was adjusted to make an angle of 45° to the axis of the tube, it was rotated by sounds whose pitches were the same or nearly so as that of the resonator.

The experimental procedure was as follows: The resonator was maintained at a constant temperature, while a Helmholtz siren generated a tone whose pitch was varied until the resonator showed a maximum deflection. The pitch of this tone was assumed to be the pitch also of the resonator. The temperature was measured by a thermo-couple inserted in the resonator, and the pitch was found from the counting device on the siren. Observations were then repeated at higher temperatures. The results gave a linear relation between N^2 and θ, which departed somewhat from the theoretical linear relation. The measurements were repeated with other instruments and arrangements of apparatus. Up to 400° C., a satisfactory linear relation was found, but above this temperature, convection currents and other disturbances made the readings uncertain. Further work is contemplated using a double resonator so that the suspended system may be removed from the heat.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS.

A GENERAL METHOD OF PRODUCING THE STROBOSCOPIC EFFECT, AND ITS APPLICATION IN THE TONODEIK.[2]

BY L. E. DODD.

THE stroboscopic effect requires two experimental arrangements: (1) a stroboscopic screen, (2) periodic illumination, or its equivalent, of this screen. While the effect has been produced heretofore by a variety of special devices, the periodic illumination, or its equivalent, of the screen has been by periodic intensity changes in a beam of light of uniform intensity over the cross-section, where the intensity of the beam periodically changes as a whole, as it does in the special case where the beam varies in intensity at the source.

[1] Rayleigh, Theory of Sound, Vol. 2, pp. 44–45.

[2] Abstract of a paper presented at the Chicago meeting of the Physical Society, December 2, 1916.

This method of periodic illumination of the screen is one of two possible general methods. The other is to impart to a beam of light of non-uniform intensity over the cross-section a back and forth periodic motion perpendicular to the direction of the beam. When such an oscillating beam falls upon a suitable stroboscopic screen the stroboscopic effect is very distinctly observed. The oscillating beam is readily provided by reflection of a stationary beam from a vibrating (phonic) mirror. Any given half-period pause of the beam results in a definite intensity at a given point on the screen, and the next following half-period pause results in a slightly different intensity at the same point, while the next following pause gives the previous intensity. Thus at the point in question there is periodically changing intensity similar to that due to flares of a manometric flame (first general method) of the same frequency as the phonic mirror causing oscillation of the non-uniform beam, and the stroboscopic effect follows. This suggested explanation accounts for observed facts.

The method of a non-uniform oscillating beam is applied in an instrument, the tonodeik, for indicating the absolute pitch of sounded tones. (See Scientific American, Nov. 4, 1916.)

State University of Iowa,
November, 1916.

A Proposed Method for the Photometry of Lights of Different Colors.—II.[1]

By Irwin G. Priest.

At the Washington meeting of the American Physical Society, April, 1915,[2] the author communicated a paper under the above title. In that communication, it was proposed that the color difference be eliminated by means of the rotatory dispersion of quartz, and the theory of computing the relative candlepowers of two lamps by the proposed method was outlined. It was stated that the method had been tried only qualitatively, the author having had no opportunity to test it quantitatively. During the past few weeks he has done some preliminary quantitative work with this method and desires to submit the essential results of these experiments in the present communication. However, it is first necessary to correct an error in the previous abstract which was not noticed until returning anew to this subject a few weeks ago. If the equation in that paper is to hold, the symbol V^{λ} (defined there as "relative visibility of light of wave-length λ") must be understood to stand, not for "visibility"[3] but for "luminosity" of the comparison source, *i. e.*, relative "visibility" times relative radiant power in the com-

[1] Abstract of a paper presented (by title) at the New York meeting of the Physical Society, December, 1916.

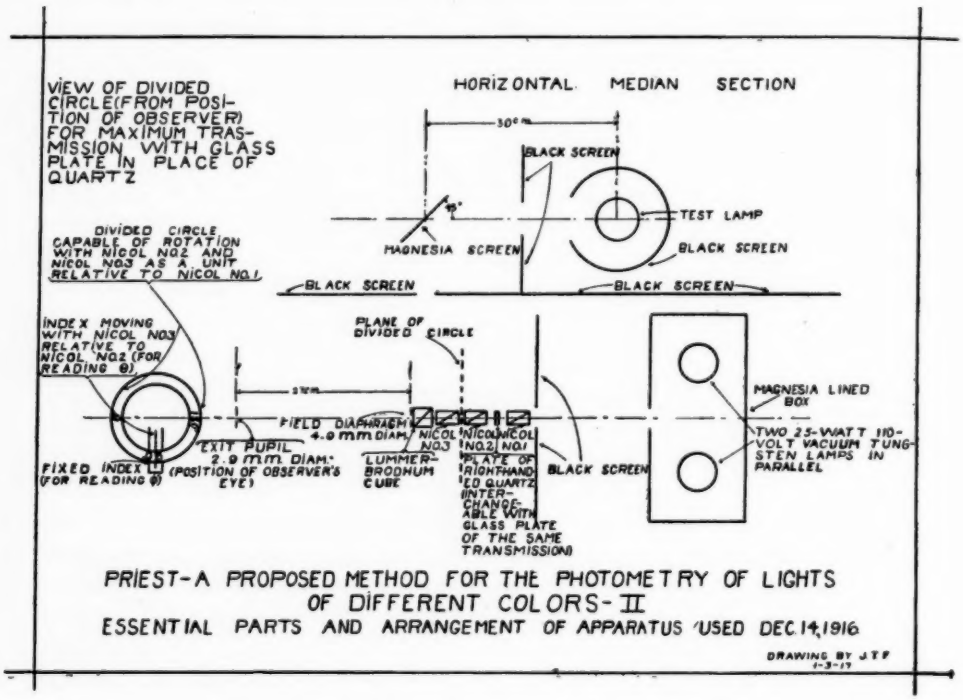
[2] Phys. Rev. (2) 6, 64.

[3] Nutting, Trans. Ill. Eng. Soc., 9, 633 (1914).

parison source.[1] Likewise on p. 66, line 4, instead of "'visibility' curve," read "luminosity curve of the comparison source."

The following is a brief statement of the essential features and results of the experiments just made.[2]

1. The apparatus and method used were essentially as described in the previous communication to the Physical Society. However, some modifications in apparatus and symbols have been introduced, so that it will be clearer to present the subject anew and without reference to the particular symbols and conventions of the previous abstract.


VIEW OF DIVIDED CIRCLE (FROM POSITION OF OBSERVER) FOR MAXIMUM TRANSMISSION WITH GLASS PLATE IN PLACE OF QUARTZ
HORIZONTAL MEDIAN SECTION
30°
BLACK SCREEN
TEST LAMP
MAGNESIA SCREEN
BLACK SCREEN
BLACK SCREEN
BLACK SCREEN
DIVIDED CIRCLE CAPABLE OF ROTATION WITH NICOL NO2 AND NICOL NO3 AS A UNIT RELATIVE TO NICOL NO1
INDEX MOVING WITH NICOL NO3 RELATIVE TO NICOL NO2 (FOR READING θ)
PLANE OF DIVIDED CIRCLE
MAGNESIA LINED BOX
FIELD DIAPHRAGM 4.9 mm DIAM.
NICOL NO3
NICOL NO2
NICOL NO1
TWO 25-WATT 110-VOLT VACUUM TUNGSTEN LAMPS IN PARALLEL
EXIT PUPIL 2.9 mm DIAM.
FIXED INDEX (FOR READING φ)
(POSITION OF OBSERVER'S EYE)
LUMMER-BRODHUM CUBE
PLATE OF RIGHTHANDED QUARTZ INTERCHANGEABLE WITH GLASS PLATE OF THE SAME TRANSMISSION
BLACK SCREEN
PRIEST-A PROPOSED METHOD FOR THE PHOTOMETRY OF LIGHTS OF DIFFERENT COLORS-II
ESSENTIAL PARTS AND ARRANGEMENT OF APPARATUS USED DEC. 14, 1916
DRAWING BY J.T.P. 1-3-17

The essential features of the apparatus are shown in the accompanying figure. The following particulars may be noted:

(*a*) The photometric field was circular, divided along a horizontal diameter. It subtended about 1° 2′ at the eye and was surrounded by a dark field.

(*b*) The maximum and minimum brightnesses of the screen illuminated by the test lamp were (computed roughly from the distance of the lamp, angle of incidence and reflecting power) 156 meter candles and 30 meter candles.

[1] In future discussions of this subject, however, the author intends to use the symbol V to represent relative "visibility" in the sense used by Nutting in his paper on Visibility of Radiation (Trans. Ill. Eng. Soc., 9, 633). Luminosity for wave-length λ will then be represented by $L_\lambda = V_\lambda E_\lambda$ where E_λ represents relative radiant power for wave-length λ.

[2] It is expected that a fuller statement of more extended work will be published later in the Scientific Papers of the Bureau of Standards.

This screen was viewed through a 2.9 mm. circular pupil by reflection in the Lummer-Brodhun cube (cemented silver strip type).

(*c*) The quartz plate was 1.000 mm. thick (this being known to within about one micron) and its surfaces were accurately perpendicular to the optic axis.

(*d*) The glass plate, interchangeable with the quartz had (by test) the same transmission as the quartz.

(*e*) The spectral energy distribution in the comparison source was established by operating it at a voltage (mean of a number of observations by different observers) giving a color match with an acetylene flame of known energy distribution,[1] in place of the test lamp (the quartz plate being replaced by glass).

2. Symbols used have meanings as follows. (Refer also to accompanying figure.)

λ, wave-length of radiation.

V, relative visibility of radiation.
E, relative radiant power, comparison source.
α, rotation of plane of polarization by 1 mm. plate of quartz perpendicular to optic axis.
} Functions of λ.

ϕ, angle read at fixed index
Θ, " " " movable "
} (see figure).

ϕ_s and Θ_s, values of ϕ and Θ observed for standard matched in color and brightness with comparison source.

ϕ_x and Θ_x, similar values for unknown candlepower.

I_s, standard candlepower.

I_x, unknown candlepower.

3. With the apparatus as shown, and, in terms of the above symbols, the general form of the equation for relative candlepower is:

$$\frac{I_x}{I_s} = \frac{\left[\int_{400}^{740} VE \sin^2(\phi_x - \alpha)d\lambda\right] \sin^2\Theta_x}{\left[\int_{400}^{740} VE \sin^2(\phi_s - \alpha)d\lambda\right] \sin^2\Theta_s}$$

If ϕ_s and Θ_s are observed with glass in the path instead of quartz, the above becomes:

$$\frac{I_x}{I_s} = \left[\frac{\int_{400}^{740} VE \sin^2(\phi_x - \alpha)d\lambda}{\int_{400}^{740} VE\, d\lambda}\right] \frac{\sin^2\Theta_x}{\sin^2\phi_s \cdot \sin^2\Theta_s},$$

which represents the condition and form used in the present experiments.

For convenience we will represent the factor

[1] Coblentz and Emerson, Sci. Paper, Bureau of Standards, No. 279.

$$\frac{\int_{400}^{740} VE \sin^2(\phi_x - \alpha)d\lambda}{\int_{400}^{740} VE\, d\lambda}$$

by R.

Assuming the spectral energy distribution data of Coblentz and Emerson for acetylene and their data for relative visibility[1] we have computed R for all values of ϕ. We have also computed R for $\phi = 65°.32$ (the value used in the present experiments) from Nutting's visibility data and the energy distribution used by him in computing visibility from luminosity. (See accompanying table.) Both of these values of R have been repeatedly determined on plots of different sizes and with different planimeters. So far as errors of computation are concerned, the mean values given here are considered accurate to about 0.2 per cent.

4. Under the above conditions, the method has been tested quantitatively to a first approximation in the following way:

One of the Bureau of Standards vacuum tungsten working standards has been used as a test lamp. (B.S. Lamp No. 1292 giving 28.46 m.h.c.p. and having an efficiency of 1.20 w.p.m.h.c. at 100.75 volts.)

The ratio of the candlepower of this lamp at 64.91 volts (3.14 w.p.m.h.c. giving a color match with a carbon lamp at 4.0 w.p.m.h.c.) to its candlepower at 99.86 volts (1.22 w.p.m.h.c.) was determined by four observers by the proposed method and also by equality of brightness in the same photometer, with the color difference present. The results obtained have been compared with the value computed from the tables of Middlekauff and Skogland.[2] These results are presented in the accompanying table. Our ratios involve the application of somewhat uncertain small apparatus corrections (for polarization) of the order of a few tenths of one per cent., and in the author's opinion they *may* be in error by as much as one or two per cent. of their value. He sees no reason, however, to suspect that the errors can be greater than this. Care has been taken to test for polarization errors in the Lummer-Brodhun cube. The voltages were determined by a calibrated Brooks deflection potentiometer used with a newly calibrated volt box and the small corrections

TABLE OF VALUES OF THE RATIO $\frac{\text{Candlepower at 64.91 Volts}}{\text{Candlepower at 99.86 Volts}}$.

applied. The voltages of the comparison and test lamps were carefully kept constant to about 0.01 volt, and the voltage on the test lamp was measured to this accuracy.

5. Qualitative test has shown that this method may be used to eliminate the color difference between the photometric standards (carbon or vacuum

[1] Mean of 125 subjects, 1916, Paper in course of publication, Scientific Paper, Bureau of Standards. Also PHY. REV. 9, 88 (Jan. 1917).

[2] Sci. Pap., Bur. of Stand., No. 238, Oct. 10, 1914.

tungsten) and gas filled tungsten lamps, by using a 1 mm. quartz plate just as in the apparatus described above.

Vac. Tung. Lamp B.S. 1292—Dec. 14, 1916.

Observer.	Color Difference Eliminated by Proposed Method $\phi = 65.32$ Degrees.			Color Difference Present.		
	Assuming Visibility and Energy Data of Coblentz and Emerson (Sci. Paper, Bureau of Standards, No. 279 and a Forthcoming Paper, Phys. Rev., p. 88, Jan. 1917). $R = 0.4532$.		Assuming Visibility Data of Nutting ("Mean Visibility," Trans. Ill. Eng. Soc. 9, 638, and Energy Data of Coblentz, Sci. Paper, Bureau of Standards, No. 156, p. 261). $R = 0.4505$.	By Equality of Brightness in Same Photometer as Used in Proposed Method, But Not Using Quartz Plate.		Computed From the Tables of Middlekauff and Skogland (Sci. Paper, Bureau of Standards, No. 238, Based on Mean Results of Other Observers Using Contrast Method).
	Ratio Mean of 10 Settings.	Dev. From Mean of All Observers.		Ratio Mean of 10 Settings.	Dev. From Mean of All Observers.	
I.G.P.....	0.1972	0.0000	Obtained from	0.1994	0.0020	
P.V.W.....	.2006	.0035	first column by	.2003	.0029	
C.G.P.....	.1944	.0028	reducing in	.1925	.0049	
H.J.M.....	.1966	.0006	proportion to change in R.	.1975	.0001	
Mean....	0.1972	0.0017 or 0.86%	0.1960	0.1974	0.0025 or 1.27%	0.1966

Conclusion.—The essential purport of this communication may be summarized as follows:

1. The quantitative experiments here reported demonstrate the practicability of the proposed method and show that (as outlined in this paper) it is not affected by any gross errors. It is thought worthy of consideration as a practical routine method of photometry.

2. The establishment of its consistency with other methods to an accuracy better than 2 per cent. will require much more experimental work. The precision and reliability of the method can no doubt be made better than that attained with the present quickly improvised apparatus.

3. The method factor R has now been accurately computed by graphic integration for 1.000 mm. of quartz for all values of ϕ using the visibility and energy distribution data of Coblentz and Emerson. Persons interested may obtain these factors by applying to the Bureau of Standards.

4. In connection with the integrating sphere, this method may afford a valuable aid in the photometry of the high-efficiency gas-filled lamps.

NATIONAL BUREAU OF STANDARDS,
December 29, 1916.
Revised February 1, 1917.

THE EFFECT OF OXYGEN ON THE PRODUCTION OF BAND AND LINE SPECTRA IN THE ELECTRIC FURNACE.[1]

BY ARTHUR S. KING.

THE several flames employed in the production of luminous vapors for spectroscopic studies involve the ignition of a gas such as hydrogen or acetylene in the presence of oxygen. The use of a plentiful supply of oxygen in a tube furnace promised to give a source in which the process is different from that in the flame, since in the furnace the heat is supplied by the incandescent tube instead of by the chemical action of the flame, while the oxygen is free to combine with the metallic vapor. Experiments were therefore carried out in which a strong stream of oxygen was passed directly through the furnace tube in which titanium or iron was being vaporized. The spectra thus obtained were compared with those given at approximately the same temperature by the furnace in vacuum. Pyrometer measurements did not show an increase of temperature resulting from the use of oxygen, but rather a slight decrease, as if the stream of fresh gas exerted some cooling effect. The bands due to the oxide were given strongly for each metal, this method being an excellent one for studying the spectra of the compounds of metals with oxygen or other gases.

With titanium, the relative intensities of the line and band spectra depended solely on the supply of oxygen. A strong stream of the gas seemed to turn all of the titanium vapor into the oxide, so that the band spectrum alone was visible, even the strongest lines being suppressed. This condition held for as high temperatures as were used, up to about 2600° C., though a temperature of about 2300° was more favorable for the band spectrum. The experiments showed that a rapid current of the gas is necessary to give oxidation of the metallic vapor, since a moderate supply, as when the furnace is operated in oxygen atmosphere, is used up by the graphite tube.

The use of iron vapor with oxygen, on the other hand, gave the line spectrum together with the oxide bands, even when a strong stream of the gas was passed through the tube. This is probably due to a less ready combination of iron vapor with oxygen than is the case with titanium. The iron spectrum was examined from λ 3200 to λ 6500 with regard to changes in the relative intensities of lines caused by the oxygen. No pronounced differences of this sort were observed, the line spectrum being practically the same except as to width of lines whether the furnace is operated in vacuum, in still air, or with a current of oxygen through the tube. A current of oxygen proved a very effective means of suppressing the "cyanogen" bands, which are given strongly by the furnace when only a small residue of air is present.

MOUNT WILSON SOLAR OBSERVATORY,
February 1, 1917.

[1] Abstract of a paper presented at the New York meeting of the American Physical Society and the A. A. A. S., December 26–30, 1916.

Experiments with the Electric Furnace on the Anomalous Dispersion of Metallic Vapors.[1]

By Arthur S. King.

THE object of the work was to make a fairly comprehensive study of the anomalous dispersion of metallic vapors, especially with regard to the spectroscopic peculiarities of lines which show the effect in different degrees.

The method of "crossed prisms" was employed, and the chief problem was the production, in a mass of metallic vapor, of a density gradient such that white light when passed through this vapor prism would undergo a change in the index of refraction near those wave-lengths which the vapor strongly absorbs. The electric furnace with a special form of tube was adapted to this purpose, the upper portion of the horizontal graphite tube being filed away from end to end of the length heated. The substance to be vaporized was placed in the trough thus formed, and a considerable density gradient was obtained in the vapor as it rose from the molten mass to the open space above. A beam of white light, narrowed by passage through a slit, traversed this vapor prism and was focused on the slit of a plane-grating spectrograph. The absorption spectrum thus obtained registered the degree of anomalous dispersion produced by each spectrum line through the curvature of the strip of continuous spectrum adjacent to the line in question.

The spectra of iron, titanium and chromium were studied through a long range of wave-length. In addition, certain lines of calcium, strontium, barium, manganese, sodium, potassium and lithium were examined. It was found possible to obtain anomalous dispersion for any line which was emitted strongly in the furnace at the temperature employed, but the conditions for the production of an effective vapor prism differed according to the character of the line concerned. Thus a low temperature of the vapor was required to give the proper distribution in the case of substances of low melting point. At higher temperatures the vapor distribution in the tube becomes more uniform and the critical condition for anomalous dispersion is lost, the spectrum showing merely wide absorption lines; although it often happens that when this stage is reached, the vapor of another substance in the tube, requiring a higher temperature to show its spectrum, gives a strong effect, so that a simultaneous condition of strong anomalous dispersion for one substance and absence of it for another may be observed. This contrast may be carried further by the production of inverted anomalous dispersion when the temperature is raised so high that lines show the opposite direction of change of refractive index to that which they showed at lower temperature. If another element whose lines require the higher temperature for their appearance is present in the tube at the same time, the striking phenomenon is presented of opposite anomalous dispersion effects for the lines of the two elements.

[1] Abstract of a paper presented at the New York meeting of the American Physical Society and the A. A. A. S., December 26–30, 1916.

The calcium line λ 4227 was thus inverted with respect to neighboring lines of chromium, the D lines of sodium with respect to barium lines, iron and chromium lines with respect to those of titanium, and manganese lines with respect to iron lines. This inversion of the effect appears to result from the particles which emit the low-temperature lines being denser in the cooler region above than near the surface of the hot tube, while the prism formed by a vapor requiring higher temperature has its denser portion below.

Such an inversion may be obtained for lines of the same element when these lines require very different temperatures for their production. This was demonstrated by the production of opposite anomalous dispersion at the same time for lines in the calcium spectrum, the effect for λ 4227 being inverted with respect to that for the H and K lines. Among the weaker calcium lines in this region, one group followed the anomalous dispersion of λ 4227 while another was affected similarly to H and K. The evidence thus seems clear that each group of emitting (and absorbing) centers may form an independent vapor prism, even when these particles belong to the same element.

The experiments showed no direct connection between the magnitude of anomalous dispersion effects and the wave-length. While for most elements the lines whose character adapts them to show the effect are in the blue and violet, the strong anomalous dispersion obtained for the D lines, barium lines in the red, and λ 6708 of lithium show that lines of strong absorption may give large effects in any region of the spectrum.

MOUNT WILSON SOLAR OBSERVATORY,
February 1, 1917.